

Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004

R.L. McCormick, T.L. Alleman, M. Ratcliff, and
L. Moens
National Renewable Energy Laboratory

R. Lawrence
Magellan Midstream Partners, LLC.

Technical Report
NREL/TP-540-38836
October 2005

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337



Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004

Technical Report

NREL/TP-540-38836

October 2005

R.L. McCormick, T.L. Alleman, M. Ratcliff, and
L. Moens
National Renewable Energy Laboratory

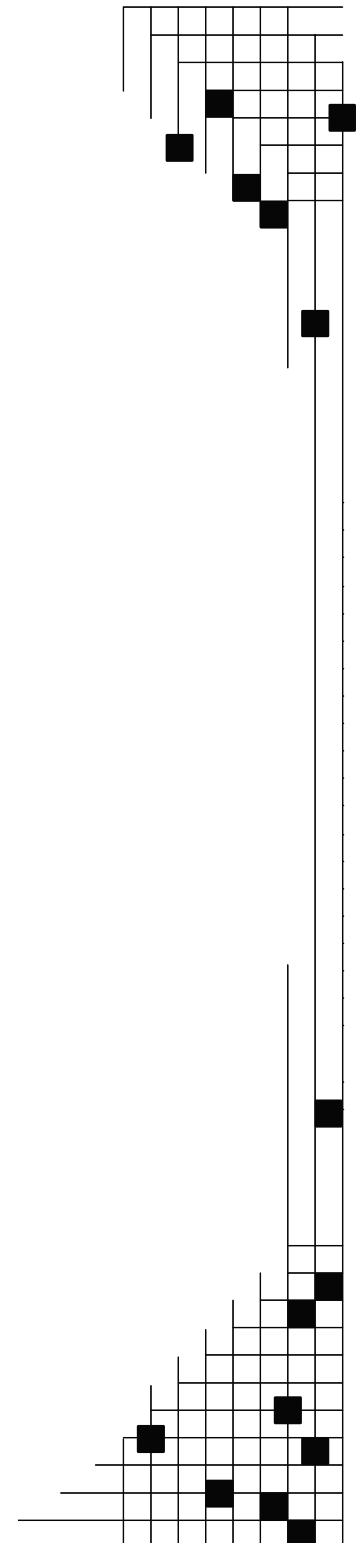
R. Lawrence
Magellan Midstream Partners, LLC.

Prepared under Task No. FC05.9400

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

Operated for the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
by Midwest Research Institute • Battelle

Contract No. DE-AC36-99-GO10337



NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Table of Contents

List of Tables	v
List of Figures	v
Acronyms and Abbreviations	vi
Executive Summary	1
Introduction	3
Survey of B100 Quality and Stability	4
Phone Survey Results	5
Initial Survey	5
Follow-up Phone Survey	5
D6751 Testing Results	6
Flash point	8
Water and sediment	8
Kinematic viscosity	8
Sulfated ash	8
Sulfur	8
Copper strip corrosion	8
Cetane number	9
Cloud point	9
Carbon residue	9
Acid number	9
Free and total glycerin	9
Phosphorus	9
Distillation temperature (T90)	10
Results of Additional Tests	10
Metals	10
Density	11
Fatty Acid Speciation	11
Testing of B100 Stability	12
Methods	12
Oxidation Stability Results	13
Oxidation Stability Discussion	16
Thermal Stability Results	21
Thermal Stability Discussion	22
B100 Summary and Discussion	24
B20 Fuel Quality Survey	27
Methods	27
Results	27
Biodiesel Content	28
Acid Number	29
Cloud Point	29
Distillation	29
Peroxide Value	30
Interfacial Tension	31

GM Water Extraction Test.....	33
Oxidation Stability by Rancimat.....	34
B20 Summary and Discussion.....	36
Conclusions and Recommendations	38
Appendix A: Mono, Di, and Tri-Glyceride Content of B100 Samples	39
Appendix B: Results of B100 FAME Analysis	41
Appendix C: Procedure for Biodiesel Testing Using DPPH Redox Indicator	43
Appendix D: Additional Modifications to the D2274 Test Method.....	44
Appendix E: Detailed Results for B20 Survey	48
Appendix F: B20 Rancimat Results.....	51
References.....	52

List of Tables

Table 1. Detailed Requirements for S15 Biodiesel Taken from ASTM D6751-03a.....	4
Table 2. Results of Initial Phone Survey	5
Table 3. Results of B100 Analysis.....	7
Table 4. Results of Additional Analyses Performed on B100 Samples	11
Table 5. Identification of Outliers Via Grubb's Test.....	26
Table 6. Tests Conducted for B20 Samples.....	27
Table 7. Mono, Di, and Tri-Glyceride Content of B100 Samples.....	40
Table 8. Results of FAME Analysis by GC-MS for B100 Samples.....	42
Table 9. D2274 Data with the Control Pad Modification.....	45
Table 10. Rancimat Induction Time, Hours.....	51

List of Figures

Figure 1. Results of analysis of selected B100 samples for FAME content.....	12
Figure 2. Rancimat (EN14112) induction time for the B100 quality survey samples.....	14
Figure 3. Frequency distribution for B100 Rancimat induction times	15
Figure 4. ASTM D2274 results for the B100 quality survey samples.....	15
Figure 5. Frequency distribution for D2274 results, B100	16
Figure 6. Comparison of results for D2274 and Rancimat oxidation stability tests	17
Figure 7. Relationship between relative antioxidant content and D2274 insolubles for different groups of biodiesel samples	18
Figure 8. Relationship between relative antioxidant content and Rancimat induction time for different groups of biodiesel samples.....	20
Figure 9. Relationship between oxidizability and Rancimat induction time for different groups of biodiesel samples.....	21
Figure 10. D6468 results for B100 quality survey samples.....	23
Figure 11. Frequency distribution for B100 Rancimat induction times	23
Figure 12. D5468 gravimetric and reflectance results for several diesel and B100 samples [10].....	24
Figure 13. Percent biodiesel content for B20 quality survey samples.....	28
Figure 14. Acid number (WLS-102) of B20 samples as a function of percent biodiesel.	29
Figure 15. Cloud point (ASTM D2500) as a function of biodiesel content for B20 survey samples.....	30
Figure 16. Distillation results (ASTM D86) for B20 quality survey samples	30
Figure 17. Peroxide value (or number) determined by ASTM D3703 for quality survey samples.....	31
Figure 18. Results of water interfacial tension measurements by ASTM D971 for B20 survey samples	32
Figure 19. Conductivity results from the GM water extraction test as a function of percent biodiesel (top) and peroxide content (bottom).....	34
Figure 20. Comparison of B20 Rancimat oxidation stability test results from SwRI and Bosch.....	35
Figure 21. Frequency distribution for B20 Rancimat stability test results (SwRI data)...	36
Figure 22. D2274 analysis	46

Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
B100	100% biodiesel
B20	20% biodiesel, 80% petrodiesel
DPPH	2,2-diphenyl-1-picrylhydrazyl
EN	European Normalization
EPA	U.S. Environmental Protection Agency
FAME	fatty acid methyl esters
GC-MS	gas chromatography-mass spectrometry
GM	General Motors
ICP-AES	inductively coupled plasma – atomic emission spectroscopy
IFT	interfacial tension
MeOH	methyl alcohol (methanol)
MSD	mass selective detector
NBB	National Biodiesel Board
NREL	National Renewable Energy Laboratory
SwRI	Southwest Research Institute
T90	temperature at which 90% of a sample has distilled (or 90% recovery temperature)

Executive Summary

This document reports results gathered from quality surveys of biodiesel and 20% biodiesel in petroleum diesel in the United States. This report also documents completion of the National Renewable Energy Laboratory's (NREL) Fiscal Year 2005 Annual Operating Plan Milestone 10.3.1, which is also Corporate Planning System Milestone 21670. These milestones support the U.S. Department of Energy (DOE), Fuels Technologies Program Multiyear Program Plan Goal of identifying fuels that can displace 5% of petroleum diesel by 2010.

For these quality surveys researchers collected 27 biodiesel (B100) samples and 50 biodiesel blend (B20) samples from blenders and distributors nationwide. These companies tended to be petroleum terminal operators or wholesalers. The following conclusions are based on the results of the B100 and B20 quality surveys conducted:

- Biodiesel blenders and distributors rely almost entirely on the biodiesel manufacturer to ensure fuel quality. Little or no downstream product testing is conducted.
- The B100 samples included 4 produced from waste oils, 1 produced from tallow, and the balance produced from soy (based on a gas chromatography – mass spectrometry analysis and cloud point).
- Of the B100 samples collected, 85% met all of the requirements of American Society for Testing and Materials (ASTM) D6751.
- Samples failing one requirement generally exhibited outlier or failing results for a second requirement.
- Distributors were not, at the time of this survey, distinguishing between S15 (15 ppm sulfur maximum) and S500 (500 ppm sulfur maximum) grades of biodiesel.
- Nearly all of the B100 samples exhibited Na+K and Mg+Ca levels below 5 ppm, a level thought to be acceptable for protection of fuel injection equipment.
- A typical U.S. biodiesel exhibits 5 mg/100 ml of deposits on the ASTM D2274 accelerated stability test and less than 1 hour induction time on the European Normalization (EN) 14112 Rancimat oxidation stability test. There is currently no oxidation stability specification for diesel fuels in the United States.
- The main factors affecting the stability of B100 are natural antioxidant content, polyunsaturated fatty ester content, and the level of mono and di-glycerides.
- An issue with splash blending of B20 blends was identified when it was discovered that 18 out of the 50 samples collected were not nominally B20. It is believed that insufficient turbulence or splashing occurred during the preparation of these blends.
- B20 samples showed high levels of peroxides, reinforcing the need for an oxidation stability requirement for B100 and perhaps for B20. While peroxide levels were not measured for B100, the formation of peroxides is well known as the initial step in fuel oxidation.
- The B20 samples exhibited low levels of water interfacial tension, indicating that water separators on engine fuel systems will not perform as intended. The high peroxide levels may contribute to the low interfacial tension.

- A typical B20 showed a less than 2 hour Rancimat (EN14112) induction time, but this may have been caused by storing the samples used in this study for 6 months prior to testing.

The following are recommendations based on the results of this study:

- Additional B100 and B20 surveys should be conducted on an ongoing basis to monitor the progress of the industry in meeting fuel quality requirements.
- A future B20 survey should be conducted in winter to allow an assessment of the impact of biodiesel blending on low-temperature performance properties.
- For future studies it is important that all analyses be performed within one month of sample collection, especially oxidation stability.
- Understanding of oxidation stability issues would be greatly enhanced by collection of field samples that have undergone significant oxidation.

Introduction

This document reports results of quality and stability surveys of biodiesel (B100) and 20% biodiesel (B20) in the United States that were performed for the U.S. Department of Energy by the National Renewable Energy Laboratory. Biodiesel is a diesel replacement fuel that is becoming increasingly popular in the United States and is being used primarily as a fuel extender at blending levels up to 20 volume percent. Approximately 36 million gallons of biodiesel were consumed in the United States during 2004 [1]. While this is only about 0.1% of the total on-road diesel market in the United States, biodiesel is still the most widely used renewable diesel fuel. Biodiesel consists of fatty acid methyl esters (FAME) produced from vegetable oils, animal fats, or waste cooking oil via transesterification with methanol. The primary feedstocks for biodiesel in the United States are soybean oil and waste cooking oil (yellow grease). Engine and vehicle manufacturers have expressed concern about the quality of this renewable fuel and the potential for poor quality fuels to cause excessive wear or premature failure of certain engine components. Potential quality issues include the presence of glycerine and glycerides, residual inorganic salts from the biodiesel production process, free fatty acids, and deposits formed from fuel oxidation.

Fuel quality specifications in the United States are set by the American Society for Testing and Materials (ASTM) International and are referred to as ASTM standards or specifications. ASTM sets these standards using a consensus process that involves stakeholders from all interested industries and segments of society who have chosen to become members of ASTM. A quality specification for 100% biodiesel (B100) has been developed (ASTM D6751). The members of ASTM are currently working to finalize a specification for 20% biodiesel blends and to change the conventional diesel fuel specification (ASTM D975) to allow inclusion of up to 5% biodiesel.

This study of biodiesel quality was conducted (1) to determine if B100 in the marketplace was meeting the D6751 specification, (2) to provide data on other properties of B100 that might be included in an updated specification (including stability), and (3) to assess the properties of B20 blends in support of the development of a new quality specification for these fuels. Magellan Midstream Partners, LLC, collected all samples during calendar year 2004. Testing was performed at the Magellan Midstream Partners, LLC laboratory, the National Renewable Energy Laboratory (NREL), and industry partner laboratories as noted.

This report documents completion of NREL Fiscal Year 2005 Annual Operating Plan Milestone 10.3.1, which is also Corporate Planning System Milestone 21670. These milestones support the DOE Fuels Technologies Program Multiyear Program Plan Goal of identifying fuels that can displace 5% of petroleum diesel by 2010.

Survey of B100 Quality and Stability

The quality specification for 100% biodiesel is ASTM D6751. This standard is for a biodiesel blendstock—biodiesel to be blended with petroleum diesel to make B20 and lower biodiesel content blends. The biodiesel standard was updated in 2003 to include both 15 ppm sulfur (S15) and 500 ppm sulfur (S500) grades (S15 grade summarized in Table 1). The purpose of each requirement of the standard is reviewed in the discussion of results.

The survey had four components: initial and follow up phone surveys of the fuel handling practices of biodiesel distributors; a sample collection and testing program to assess biodiesel conformance with ASTM D6751; and an assessment of biodiesel stability. Each sample was subjected to all of the tests outlined in the D6751 specification. Analyses were also conducted for several metals of interest, for density, and for FAME make up. In addition, the following stability methods were employed:

- European Normalization (EN) 14112 (Rancimat test)
- ASTM D2274 Standard Test Method for Oxidation Stability of Distillate Fuel Oil
- ASTM D6468 Standard Test Method for High Temperature Stability of Distillate Fuels.

Table 1. Detailed Requirements for S15 Biodiesel Taken from ASTM D6751-03a

Property	Method	Limits	Units
Flash Point	D93	100.0 min	°C
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40°C	D445	1.9 - 6.0	mm ² /sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur*	D5453	0.0015 max.	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane Number	D613	47 min.	
Cloud Point	D2500	Report to Customer	°C
Carbon Residue**	D4530	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus content	D4951	0.001 max.	% max
Distillation temperature, T90***	D1160	360 max.	°C

*The specification also includes a higher sulfur grade of biodiesel, S500, that allows 0.05 wt% sulfur but all other requirements are identical.

**Carbon residue shall be run on the 100 % sample.

*** Atmospheric equivalent temperature

Phone Survey Results

Initial Survey

For this phone survey, a list of biodiesel blenders and sellers was obtained from the National Biodiesel Board website (www.biodiesel.org). In addition, contacts for several other blenders were provided by Magellan. The survey consisted of a series of questions regarding the controls established for assuring that consistent quality products are delivered to customers. The questions and a tally of the responses follow in Table 2.

The majority of the respondents did not have contractual terms with suppliers regarding product quality, and did not receive analytical reports or perform subsequent product testing. Even in this majority, the general sentiment was that the product received is of satisfactory quality and met any applicable specifications. Of the 10 respondents who perform inspection upon receipt, only two perform any actual quantitative tests. The others simply visually examine the product.

Thus, the burden for product quality rests with the producer. After the product has left the producer, there is little surveillance of product quality and thus no established mechanism for identifying poor quality or contaminated fuel. Generally the blending procedures are the same as those used for blending two or more petroleum products with no special provisions for biodiesel.

One respondent requires the delivery of only “vegetable-based” biodiesel in the winter. Another injects an anti-gel additive in the winter. The majority of the respondents did not require or request product from a particular producer and did not know the identity of the producers for individual batches.

Table 2. Results of Initial Phone Survey

	Yes	No	Don't Know
1) Do you purchase biodiesel from only one marketer?	21	8	
2) Is your biodiesel supplied from multiple producers?	16	8	4
3) Do your contracts specify receipt of a type of biodiesel, e.g., soy?	6	18	5
4) Are specifications included in a purchasing agreement?	4	20	5
5) Do you receive an analytical report with each batch of biodiesel?	12	16	1
6) Do you perform any inspection upon receipt of each batch?	10	19	
7) Do you blend biodiesel w/ petroleum diesel?	20	9	
8) If yes to '7', do you have formal blending procedures?	16	4	
Of the respondents, 25 received delivery by truck, 2 by rail, 1 both, and 1 drums.			

Follow-up Phone Survey

A second survey was conducted after the sample-testing element of this project was completed. This survey focused on identification of problems that the distributors had encountered and the length of storage periods. The questions and responses follow:

1. Have you encountered any problems handling biodiesel?
Yes 5 No 14
2. If yes, what was the nature of the problem(s)?
Cold flow upon receipt 3
Haze with sediment 1
Dirty delivery truck 1
3. Have you received any customer complaints?
Yes 3 No 16
4. If yes, what was the nature of the complaint?
Customer stored in steel drums outside resulting in water contamination
Customer blended with an additive that made it look like rice pudding
Lost power and engine stalled with a depressed clutch. Operating on B80 to B100 depending on how much diesel fuel is in the tank when the customer adds B100 to the tank.
5. Has anyone complained of a filter plugging problem or injector fouling?
Yes 1 No 18
6. If yes, what do you think caused the problem?
Not sure, thinks it was water and sediment
7. What is the frequency at which the material in your tank is replaced (frequency of turns)?

< 1 wk	1 to 4 wks	5 to 8 wks	> 8 wks
2	8	3	1
8. How do you utilize your tank, e.g., fill completely and then empty?

Fill then empties	Maintains volume
8	6
9. Do you retain samples of each product receipt?
Yes 7 No 12

D6751 Testing Results

Twenty-seven samples were obtained nationwide from biodiesel blenders and sellers. Each sample was subjected to all of the tests outlined in the ASTM D6751-03a specification. Results for each of the samples are shown in Table 3 and indicate that 4 out of 27 samples, or roughly 15%, exceeded one or more of the limitations. Each requirement is discussed individually in the following paragraphs.

Table 3. Results of B100 Analysis

All samples also met the water and sediment (D2709) requirement and were 1A for copper corrosion. Italics indicate properties that exceed D6751-03a limits.

Sample ID	Flash Point	Viscosity	Sulfated Ash	Sulfur	Cetane	Cloud Point	Carbon Residue	Acid No.	Free Glycerine	Total Glycerin	Phosphorus	Distillation T90
Test	D93	D445	D874	D5453	D613	D2500	D524b	D664	D6584	D6584	D4951	D1160
Limit	>130°C	1.9-6.0 mm ² /s	0.020 wt%	0.05 wt%	47 min	°C	0.05 wt%	0.8 mgKOH/g	0.02 wt%	0.24 wt%	0.001 wt%	360 max
A	147	4.489	0.000	0.00029	54.7	2	<0.010	0.25	0.003	0.208	0.0006	354
B	153	4.128	0.000	0.00036	49.6	0	<0.010	0.60	0.002	0.202	0.0008	354
C	133	4.085	0.005	0.00003	53.7	-2	<0.010	0.33	0.003	0.147	0.0005	352
D	143	4.361	0.015	0.00827	57.7	-1	0.015	0.24	0.004	0.239	0.0030	355
E	133	4.153	0.003	0.00268	53.7	-1	<0.010	0.59	0.003	0.190	0.0007	354
F	147	3.976	0.003	0.00134	58.3	-1	<0.010	0.11	0.012	0.019	0.0007	352
G	157	4.784	0.001	0.00012	48.0	-1	0.015	0.16	0.014	1.23	0.0005	357
H	>190	3.991	0.000	0.00026	57.2	-1	<0.010	0.05	0.004	0.032	0.0005	352
I	156	4.099	0.000	0.00003	54.3	-1	<0.010	0.97	0.006	0.023	0.0002	352
J	>190	4.145	0.000	0.00069	54.4	0	<0.010	0.35	0.004	0.171	0.0003	352
K	>190	4.245	0.003	0.00115	51.9	0	0.018	0.76	0.003	0.192	0.0006	352
L	154	3.970	0.000	0.00032	54.7	-1	<0.010	0.05	0.004	0.037	0.0010	351
N	162	4.159	0.000	0.00105	48.8	0	<0.010	0.48	0.004	0.211	0.0008	354
O	152	4.093	0.001	0.00012	51.5	1	<0.010	0.70	0.003	0.198	0.0010	354
P	168	3.927	0.000	0.00005	55.1	-2	<0.010	0.03	0.002	0.011	0.0003	352
Q	152	4.107	0.003	0.00010	54.0	0	<0.010	0.34	0.008	0.067	0.0013*	352
R	172	4.010	0.003	0.00035	56.4	-1	<0.010	0.02	0.002	0.013	0.0002	351
S	154	3.928	0.005	0.00089	56.1	-1	<0.010	0.02	0.006	0.020	0.0004	351
T	>190	4.560	0.011	0.00145	56.3	2	0.043	1.38	0.018	0.317	0.0000	354
U	174	4.122	0.001	0.00006	57.6	-1	<0.010	0.65	0.004	0.195	0.0002	352
V	190	4.800	0.000	0.00127	54.2	5	<0.010	0.42	0.009	0.187	0.0000	352
W	161	4.134	0.000	0.00044	52.3	-1	<0.010	0.48	0.005	0.025	0.0001	352
X	>190	4.100	0.002	0.00089	52.7	-2	<0.010	0.54	0.011	0.196	0.0002	352
Y	159	4.706	0.000	0.00081	65.0	14	<0.010	0.48	0.006	0.058	0.0004	351
Z	161	4.123	0.001	0.00014	53.3	-2	<0.010	0.34	0.001	0.022	0.0007	351
AA	165	4.610	0.000	0.00048	56.0	8	<0.010	0.52	0.005	0.102	0.0000	351
BB	>190	4.087	0.001	0.00067	54.8	-1	0.013	0.35	0.014	0.025	0.0006	351

*Based on rounding to 0.001 wt%, this sample meets the phosphorus requirement.

Flash point

This requirement ensures that the methanol used in production is completely removed from the fuel, because of both fire safety concerns and the corrosive nature of methanol. The flash point for the samples ranged from 133°C to greater than 190°C; all samples met the requirement of 130°C minimum.

Water and sediment

This test method determines the sum of free water and sediment. Free water is undesirable because it may promote microbial growth and corrode fuel system components. Sediment or solid impurities are undesirable because of their potential to cause excessive wear in fuel injection equipment. All samples met the requirement 0.05 vol% maximum.

Kinematic viscosity

Adequate viscosity is required for lubrication and to prevent leakage in metal/metal seals, but viscosity must not be so high as to cause seizure of parts, particularly under low-temperature conditions. High-viscosity fuel can also cause higher injection pressures leading to increased wear and shorter equipment life. Viscosity of the samples ranged from 3.927 to 4.800 mm²/s, with all samples tested meeting the requirement of 1.9-6.0 mm²/s.

Sulfated ash

The sulfated ash requirement is intended to limit the amount of potassium, sodium, magnesium, and calcium in the finished biodiesel fuel. These metals can contribute to injector, fuel pump, piston and ring wear, engine deposits, and filter plugging. These impurities may be introduced from process chemicals used in biodiesel manufacture. Measured values ranged from zero (below detection limit) to 0.015 wt%, with all samples meeting the requirement of 0.020 wt% maximum.

Sulfur

The sulfur requirement is intended to mirror that in ASTM D975 (Standard Specification for Diesel Fuel Oils) and to meet the U.S. Environmental Protection Agency (EPA) requirements for on-road diesel fuel. Thus, the sulfur limit as of this writing is 0.05 wt% (or 500 ppm, denoted as S500) for on-road diesel fuel, but will be dropped to 0.0015 wt% (or 15 ppm, denoted as S15) beginning in September 2006. All samples met the 500 ppm requirement, however, two soy-derived samples (D and E) exhibited sulfur in excess of 15 ppm. The soy oil used to produce these fuels is inherently low in sulfur (much lower than 15 ppm), thus it seems likely that these samples were contaminated with small quantities of higher sulfur materials during handling and transport.

Copper strip corrosion

Corrosion is of concern because of potential damage to copper components of fuel systems, but also because dissolved copper can catalyze oxidation reactions leading to the formation of deposits and corrosive free acids. This requirement mirrors the D975 requirement for conventional diesel and is designed to ensure that biodiesel is equally compatible with and resistant to oxidation by, copper. All biodiesel samples tested exhibited a 1A rating on this test, easily meeting the standard of 3 maximum.

Cetane number

An adequate cetane number is required for ignition and operability. Conventional diesel in the United States is required to have a minimum cetane number of 40. Biodiesel produced in the United States has a significantly higher cetane number, and therefore, the specification limit was set at 47 minimum. All samples tested exceeded this level, easily meeting the standard. In fact, the mean, median, and mode of the cetane number results are all roughly 54.5.

Cloud point

There is no specific cloud point requirement in D6751, only a requirement that it be measured and reported. The purpose of a cloud point specification is to ensure operability at low temperatures. The soy-derived samples are all in the range of -2°C to 1°C , with yellow grease and tallow-derived fuels exhibiting higher values. Based on cloud point (and confirmed by FAME analysis reported below) the following samples were likely produced from yellow grease or waste oil: A, T, V, and AA. Sample Y was produced from beef tallow.

Carbon residue

This test provides an estimate of the carbon depositing tendencies of a fuel and is designed to prevent the formation of combustion chamber deposits. All samples tested met this requirement of 0.05 wt% maximum. Sample T had the highest value of 0.043 wt%, and also failed the acid number and total glycerin tests. High levels of glycerides are expected to contribute to engine deposit formation and hence to a higher carbon residue.

Acid number

This test measures the presence of corrosive free fatty acids and oxidation products. Two of the samples tested exhibited acid numbers above the maximum limit of 0.8 mg KOH/g. For Sample I there are no obvious clues in the data as to why acid number is high, and this sample may have undergone some oxidation. For Sample T, total glycerin is also high, and carbon residue is the highest value observed.

Free and total glycerin

Total glycerin includes the sum of free glycerin and mono, di, and tri-glycerides, all reported as mass percent glycerin and determined by gas chromatography. Results for the individual glycerides can be found in Appendix A. Free glycerin can cause fuel separation and materials compatibility problems. Glycerides have much higher boiling points than biodiesel or conventional diesel fuel, and can lead to engine deposits and durability problems. All samples met the free glycerin requirement of 0.02 wt% maximum, however, two samples failed the total glycerin requirement of 0.24 wt% maximum. One of these is Sample T, as already noted. In addition, Sample G exhibited high total glycerin but met all other requirements.

Phosphorus

The intent of this requirement is to protect exhaust catalysts, which are becoming more and more common on diesel equipment. Sample D exhibited 0.003 weight percent phosphorus and thus failed to meet the requirement of 0.001 weight percent maximum (10 ppm). Given the high sulfur content of this sample, it is possible that it was contaminated with a small amount of motor oil, which contains both sulfur and phosphorus as part of the antiwear additive package. Metals analysis (discussed in the following section of this report) supports this contention.

Distillation temperature (T90)

This requirement ensures that the biodiesel has not been altered with significant amounts of high boiling components, such as used motor oil. All biodiesel samples exhibited T90 in a narrow range from 351°C to 357°C, and thus met this requirement of 360°C maximum. As noted above, Sample D appeared to be contaminated with a small amount of motor oil. The amount of oil was enough to cause the sample to be out of specification on phosphorus, but not enough to influence the T90.

Results of Additional Tests

A number of additional tests that are not included in ASTM D6751 were conducted to provide additional information and an assessment of the potential usefulness of these tests as added requirements in D6751.

Metals

The presence of metals in the biodiesel can cause operability problems due to formation of deposits and poisoning of emission control devices, or can catalyze reactions that cause undesired products. The metals of interest include sodium (Na) and potassium (K), used as catalysts in biodiesel production; and magnesium (Mg) and calcium (Ca), used in adsorbents for purifying biodiesel. Fuel injection equipment manufacturers have proposed to limit the content of Na+K and of Mg+Ca to 5 ppm each. Additionally, we tested for copper (Cu), iron (Fe), and zinc (Zn). Each of these metals can catalyze oxidation, however, copper and zinc in particular can be highly active for initiating oxidation of polyunsaturated methyl esters [2]. Zinc can enter the fuel if it is contaminated by lube oil. Metals analyses were performed in conjunction with testing of the samples for phosphorus content via ASTM D4951 by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and results are shown in Table 4.

For all samples potassium levels were below detection limits. All samples but one contained less than 5 ppm of sodium. The high-sodium sample is Sample T, which also failed D6751 requirements for acid number and total glycerin. Clearly this low-quality sample was not adequately washed for removal of residual catalyst. B100 samples also exhibited generally low levels of magnesium and calcium. However, Sample D exhibits high levels of both of these metals. This sample also failed the D6751 phosphorus limit and exhibited 83 ppm of sulfur. Table 5 also shows this sample having high levels of zinc. All of these features are consistent with contamination by lube oil. For other samples with moderately elevated calcium content (5 or 6 ppm), the source is likely the use of hard water for product washing.

Iron levels ranged from 1 to 12 ppm. Dissolved iron can be a potent oxidation catalyst and thus may contribute to biodiesel instability. Copper content was typically 0-2 ppm, but one sample (N) exhibited 5 ppm. Other than sample D, four samples had zinc content in the 4-8 ppm range. However, it is not known if these levels are high enough to cause stability issues. The impact of metals content on stability will be explored in the following section of this chapter.

Density

Density was also measured and is reported in Table 4. The density of B100 is typically 0.88 g/ml, significantly higher than is typical of petroleum diesel, which ranges from 0.84 to 0.86 g/ml.

Table 4. Results of Additional Analyses Performed on B100 Samples

Results of additional analyses performed on B100 samples
(a measured value of 0 indicates below detection limit).

Sample ID	Calcium ICP D4951 ppm	Copper ICP D4951 ppm	Iron ICP D4951 ppm	Magnesium ICP D4951 ppm	Potassium ICP D4951 ppm	Sodium ICP D4951 ppm	Zinc ICP D4951 ppm	Density D4052 @ 60 °F (g/mL)
A	2	0	1	0	0	3	6	0.8826
B	4	0	1	0	0	2	4	0.8826
C	0	0	1	0	0	1	1	0.8845
D	35	0	1	7	0	2	38	0.8862
E	6	0	1	0	0	1	4	0.8845
F	0	0	2	0	0	0	1	0.8835
G	0	2	1	0	0	2	0	0.8888
H	1	0	1	0	0	0	0	0.8847
I	0	0	3	0	0	0	0	0.8838
J	2	2	1	1	0	1	2	0.8850
K	0	1	12	0	0	2	2	0.8852
L	0	0	1	0	0	0	0	0.8837
N	1	5	1	0	0	2	2	0.8847
O	0	0	1	0	0	3	0	0.8846
P	0	0	1	0	0	0	0	0.8836
Q	5	0	2	0	0	0	1	0.8839
R	0	1	1	0	0	0	0	0.8838
S	0	0	1	0	0	0	0	0.8833
T	1	0	9	1	0	37	0	0.8826
U	0	0	1	0	0	1	0	0.8827
V	0	0	1	0	0	1	5	0.8798
W	2	1	4	0	0	0	1	0.8838
X	2	0	2	0	0	2	8	0.8831
Y	1	0	1	0	0	0	0	0.8751
Z	1	1	1	0	0	1	1	0.8823
AA	1	0	1	0	0	0	0	0.8768
BB	0	1	3	0	0	0	2	0.8817

Fatty Acid Speciation

A subset of the biodiesel samples was analyzed by gas chromatography with mass spectrometric detection (GC-MS). Method details and a complete table of results are found in Appendix B. The FAME results are summarized in Figure 1. The results show obvious similarities between most of the soy samples (samples B through U). Sample Z is also soy-derived but contains lower C18:3[†] and higher C18:2 than the others. The sample A was originally thought to be soy methyl esters,

[†] The notation Cxx:y indicates a methyl ester with an xx carbon atom fatty acid chain containing y double bonds. For example, methyl oleate or CH₃(CH₂)₇CH=CH(CH₂)₇COOCH₃ is denoted C18:1.

but contains higher amounts of methyl palmitate and methyl stearate than the soy-derived samples; therefore, it is most likely derived from waste cooking oil. The oleate/linoleate ratio is higher as well (0.77 versus a more typical 0.44). The data suggest that this sample may contain methyl esters from non-soy feedstocks. The other waste grease samples (V and AA) contain relatively high amounts of saturated FAME and otherwise indicate variability in composition as would be expected. Sample T is also likely derived from waste grease given its slightly high cloud point. Sample Y is derived from beef tallow and contains high concentrations of saturated C14, C16, and C18 as expected.

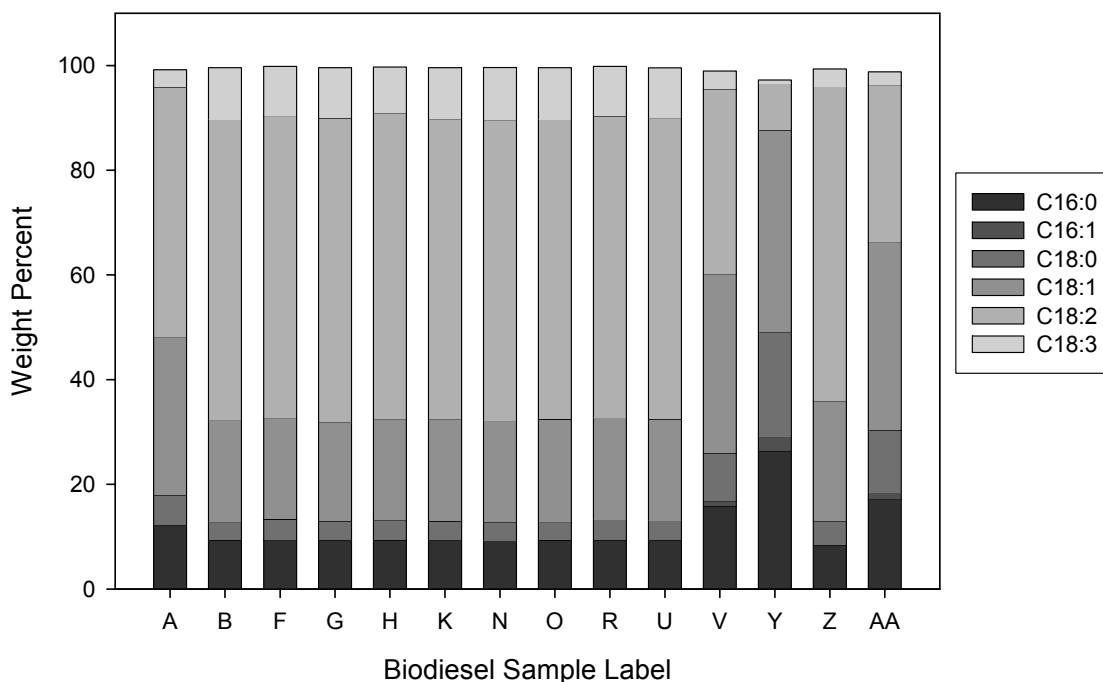


Figure 1. Results of analysis of selected B100 samples for FAME content
Only species with concentration greater than 1 wt% shown; detailed analyses in Appendix B.

Testing of B100 Stability

Biodiesel, without modifications or treatment with additives, is inherently less stable than a typical petroleum diesel. However, there are no limits for stability in the accepted industry standard for biodiesel, ASTM D6751. Companies that transport and store biodiesel are concerned that the fuel does not form sediment in storage. They are also interested in knowing what precautions can be taken to ensure satisfactory storage characteristics. Vehicle and equipment operators need assurances that sediment and gum do not form during use. For these reasons, the B100 survey was expanded to examine the stability characteristics of fuels in commerce and take a more in-depth evaluation of the merits of various stability test methods.

Methods

Three accelerated stability test methods were performed on each of the samples collected for the survey: ASTM D2274, Standard Test Method, Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method), ASTM D6468, Test Method for High Temperature Stability of Distillate Fuels, and EN14112 (Rancimat). D2274 and the Rancimat test are designed to predict

storage stability, and the D6468 test provides an indication of thermal or in-use stability. A simple procedure for measuring the total antioxidant content of a biodiesel sample was developed and applied in this study [3], and method details are given in Appendix C.

In the Rancimat method, the sample is exposed to a stream of air at 110°C. The stream of air carries volatile carboxylic acids (primarily formic acid [4]) that are formed in the oxidation reaction into an absorber section that contains demineralized water. The amount of acids that are captured is quantified by measuring the increase in the conductivity of the water. The reported measurement is the induction period, which is the amount of time from the beginning of the air purge until a sharp increase in the conductivity is observed. The induction period is reported in terms of hours.

In the D2274 method, the sample is heated to 95°C and exposed to pure oxygen for a period of 16 hours. After this reaction time, the amount of sediment (filterable insolubles) and gum (adherent insolubles) are determined. The total of these two reaction products is classified as Total Insolubles and is reported in terms of milligrams per 100 milliliters of sample. The filtration element of the D2274 test method is generally revised for biodiesel due to the tendency for biodiesel to dissolve or swell the filter pads that are called for in the method. Normally a Teflon filter is used. In this project, glass fiber filters were used. Irrespective of the filtration medium, the nature of the material that is retained on the filter poses a problem. Normally the filterable insolubles that are generated in the reaction appear as a granular material on the filter pad. The material generated in this project was a rather viscous material that appeared to migrate through the filter pad with sufficient vacuum and time. For this reason, the analysts attempted to keep the duration of the filtration procedure as consistent as possible.

The D6468 test exposes the sample to air at a temperature of 150°C for a period of 180 minutes. After this reaction period, the sediment that is formed during the reaction is captured on a filter paper, and the reflectance of the sediment of a particular light source is measured. In this project, after the reflectance was measured the amount of sediment on the filter paper was determined gravimetrically, and the acidity of the sample was determined.

Oxidation Stability Results

The data from the Rancimat tests were widely varied ranging from 0.1 to 6.0 hours, as shown in Figure 2, and a frequency distribution is shown in Figure 3. The European standard for biodiesel has a stability specification of a minimum induction period of 6.0 hours [5]. Only one sample in this sample set would pass the European specification—sample AA. The majority of the samples exhibited an induction period of less than one hour. Additionally, there was no correlation of the Rancimat results with the initial acid values of the samples (correlation coefficient of 0.05).

The results for the D2274 test are shown in Figure 4 for total insolubles. The reaction generated equal quantities of filterable and adherent insolubles. The average amount of filterables was 2.46 mg/100mL, and the average amount of adherent insolubles was 2.47 mg/100mL. The standard deviations for the filterables and adherent insolubles were 1.6 and 1.2, respectively. Figure 5 shows a frequency distribution for total insolubles. A typical biodiesel produced on the order of 5 mg/100 ml.

With the goal of improving accuracy and precision, a number of potential modifications to the D2274 test method were investigated. This activity is described in Appendix D. In addition, in another project performed for NREL [6], it has been shown that precipitation of insolubles with a non-polar solvent such as heptane can approximately double the amount of insolubles collected, potentially improving both method precision and accuracy.

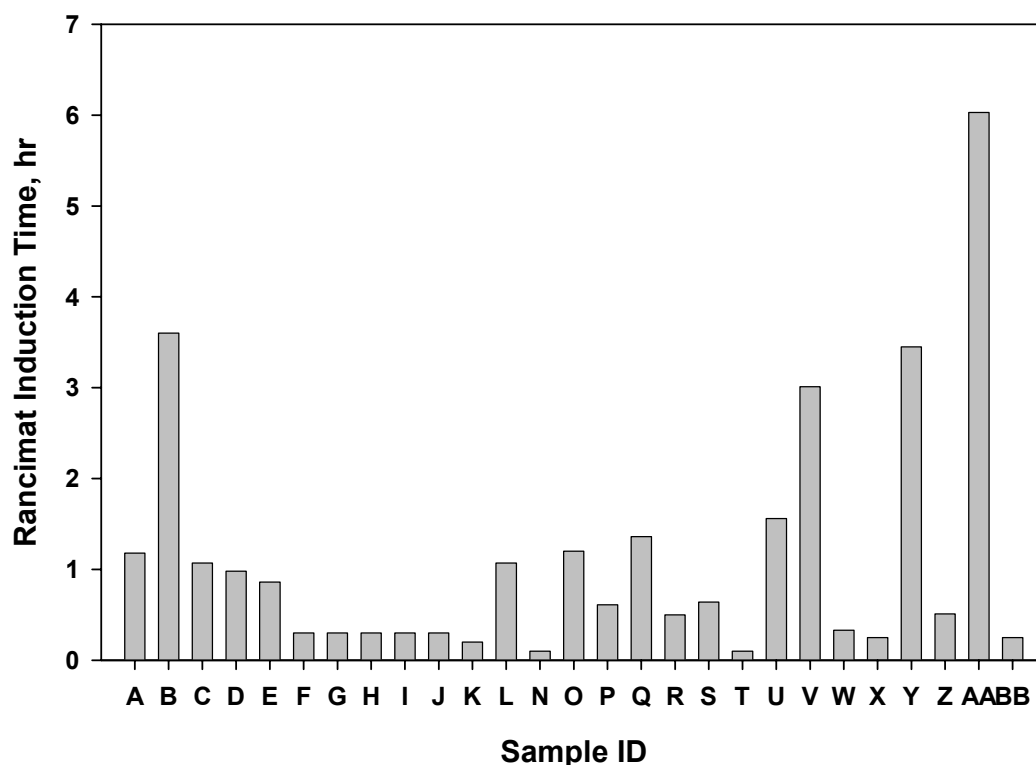


Figure 2. Rancimat (EN14112) induction time for the B100 quality survey samples

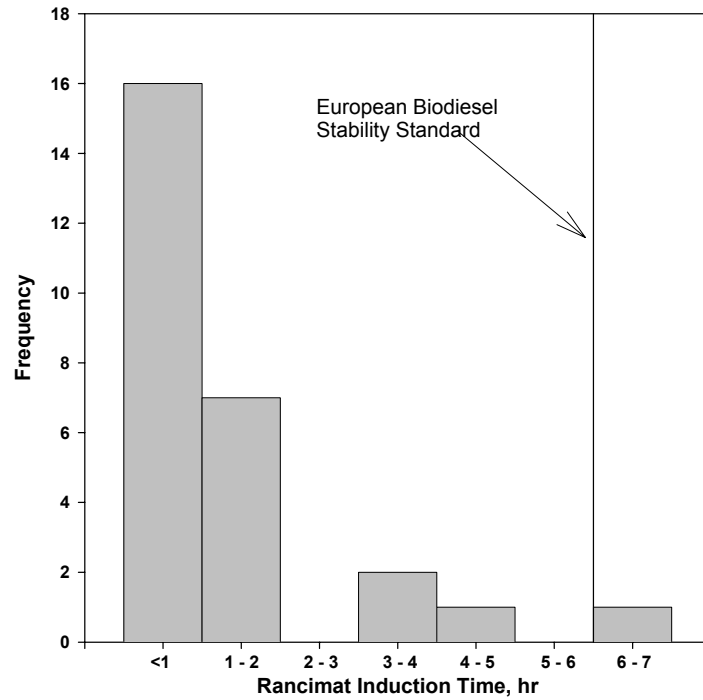


Figure 3. Frequency distribution for B100 Rancimat induction times

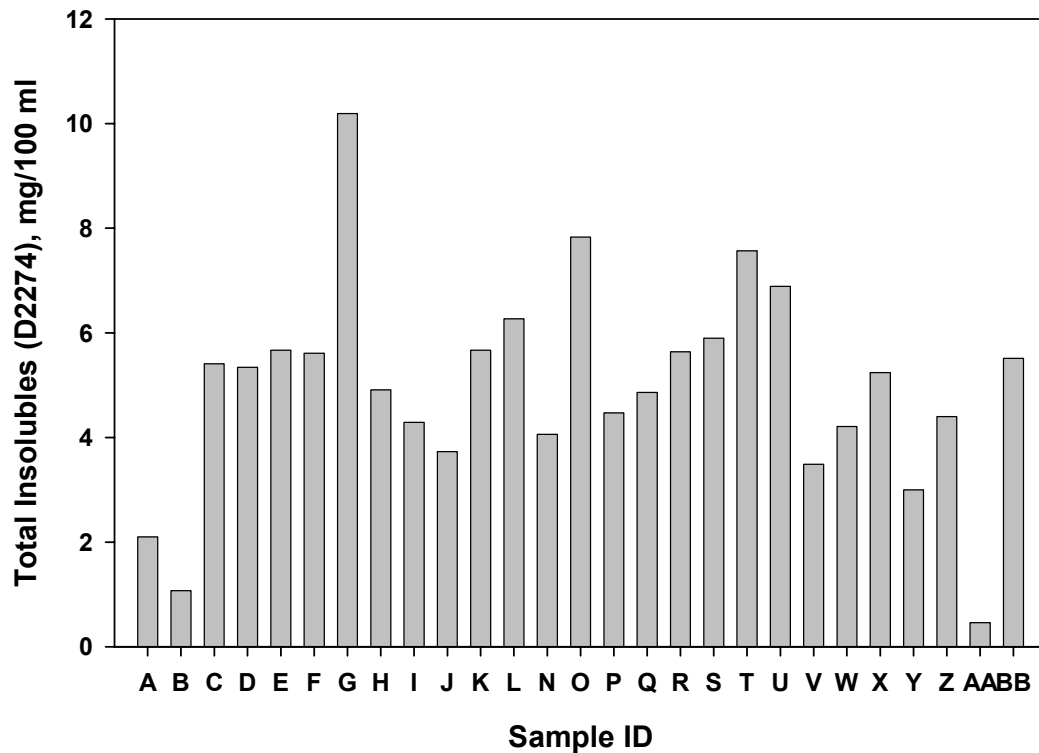


Figure 4. ASTM D2274 results for the B100 quality survey samples

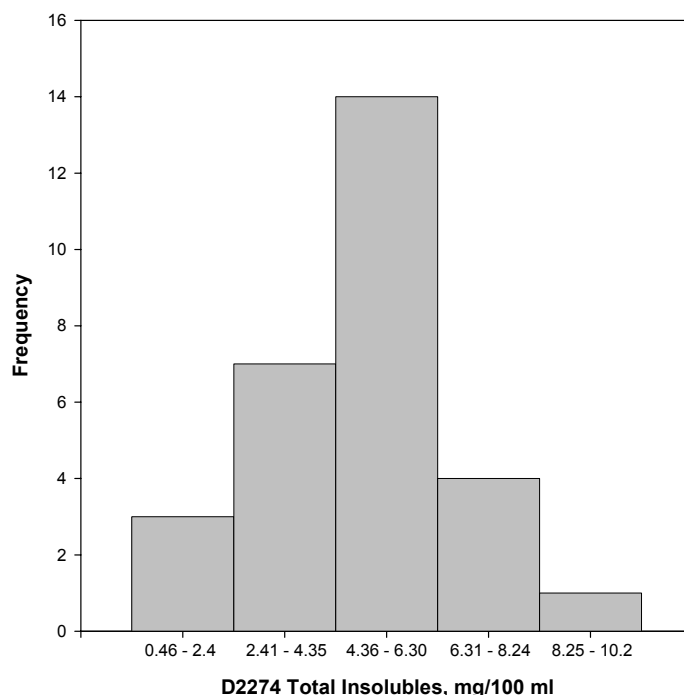


Figure 5. Frequency distribution for D2274 results, B100

Oxidation Stability Discussion

A comparison of Figures 3 and 5 indicates that Rancimat and D2274 results are not well correlated, as is confirmed in Figure 6. While there is a rough inverse correlation, it is clear that some samples with short induction times also have fairly low levels of insolubles (note the sample with approximately 1 hour Rancimat and 2 mg/100 ml of insolubles), and samples with long induction times can have insolubles as high as 4 mg/100 ml. This highlights the fact that these two test methods have a very different premise. The D2274 method exposes the fuel for a long period of time (16 hrs) to highly oxidizing conditions (oxygen at 95°C). The inherent potential of the material being tested to form polymers under these conditions is measured. The Rancimat test, on the other hand, measures the length of time at 110°C in air before volatile acidic oxidation products begin to form. Thus the Rancimat test seems more suited to predicting how long a material can withstand oxidative conditions, not its inherent tendency to form polymers.

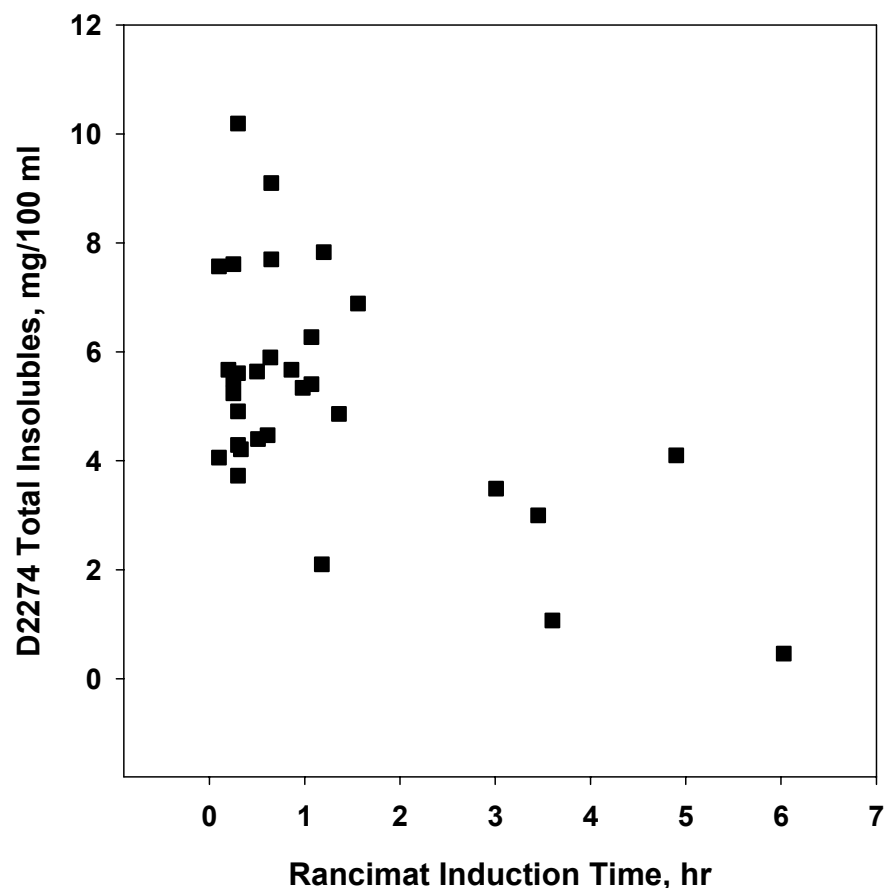


Figure 6. Comparison of results for D2274 and Rancimat oxidation stability tests

Given the relatively extensive characterization of these samples, it is also possible to utilize the data to assess the factors that are important in oxidation stability for biodiesel. One potential factor mentioned above is metals content. However, for the samples tested here, there was no correlation between D2274 results or Rancimat results, and the concentrations of copper, iron, zinc, or the sum of all three metals in these samples.

There is a significant effect of antioxidant content on the D2274 test results, as shown in Figure 7. The first important feature of the data shown in this figure is that the antioxidant content of biodiesel had a range of roughly one order of magnitude (less than 0.5 to nearly 6), and that for the soy biodiesel samples, insoluble formation can also vary by nearly a factor of 10. For the soy diesel samples (which all met D6751 and have very similar C18:2 and C18:3 content) the relative antioxidant content was a generally good predictor of insolubles formation. Results for the more highly saturated grease and tallow-derived samples generally fall below the line suggested by the soy-antioxidant relationship. Finally, samples with total glycerin content exceeding the limit defined in ASTM D6751 exhibit significantly higher levels of insolubles formation than anticipated based on their antioxidant content or polyunsaturated fatty ester content.

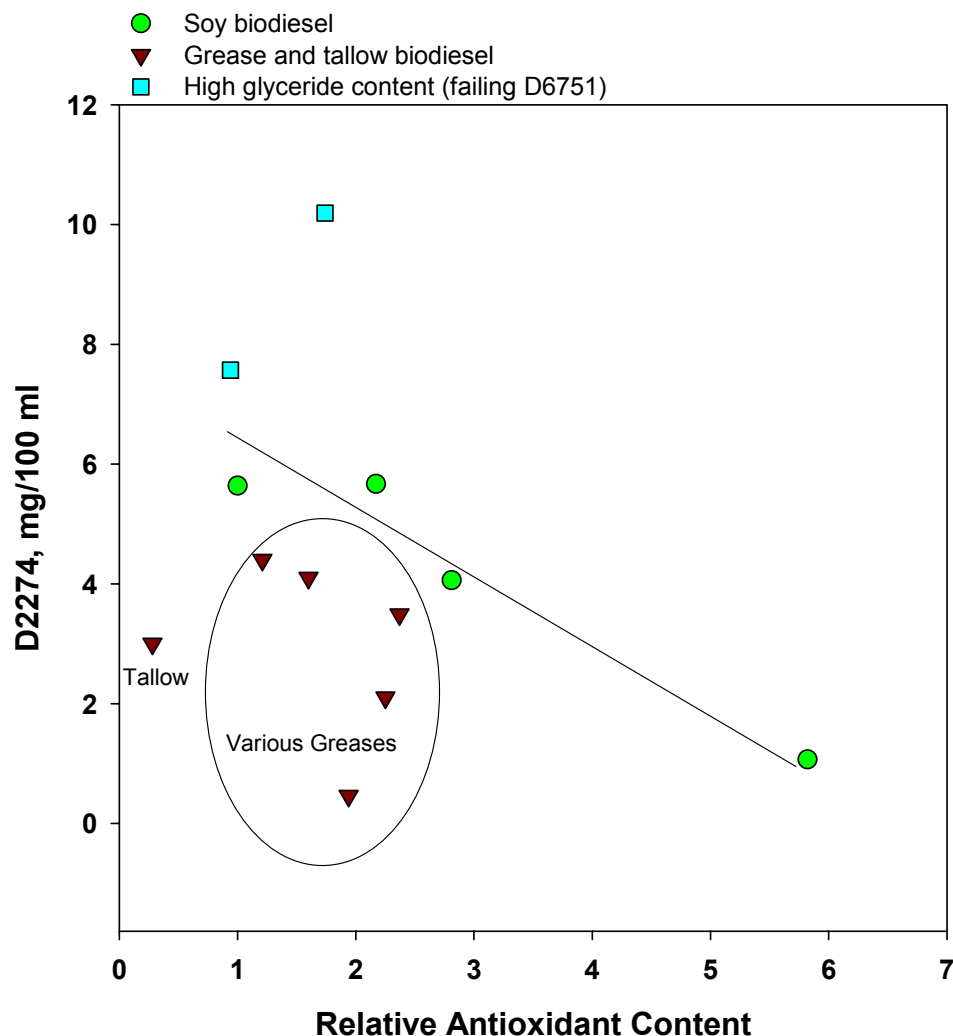


Figure 7. Relationship between relative antioxidant content and D2274 insolubles for different groups of biodiesel samples

A plot similar to Figure 7, but for Rancimat induction time, is shown in Figure 8. Here the effect of antioxidant content, total glycerin content, and polyunsaturated content is not as clear; although more highly saturated samples and samples with higher antioxidant content do exhibit longer induction time. Another way to examine these data is to use some measure of unsaturation as the dependent variable. Such a measure is the oxidizability [7], defined as:

$$\text{Oxidizability} = [0.02(\% \text{ oleic}) + (\% \text{ linoleic}) + 2(\% \text{ linolenic})]/100$$

This derived parameter applies only to biodiesel or fat containing predominantly 18 carbon fatty acid chains, such as the samples examined here. The coefficients for oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) fatty esters are proportional to the relative rates of oxidation of these compounds [8]. The relationship between Rancimat induction time and oxidizability is shown in Figure 9. All of the soy biodiesel samples examined have nearly the same fatty acid ester composition and hence the same oxidizability. Hence this parameter is not successful at

discriminating between these samples. For the grease and tallow-based biodiesel, however, oxidizability seems to be a reasonable predictor of Rancimat induction time. A similar plot for D2274 insolubles could be made.

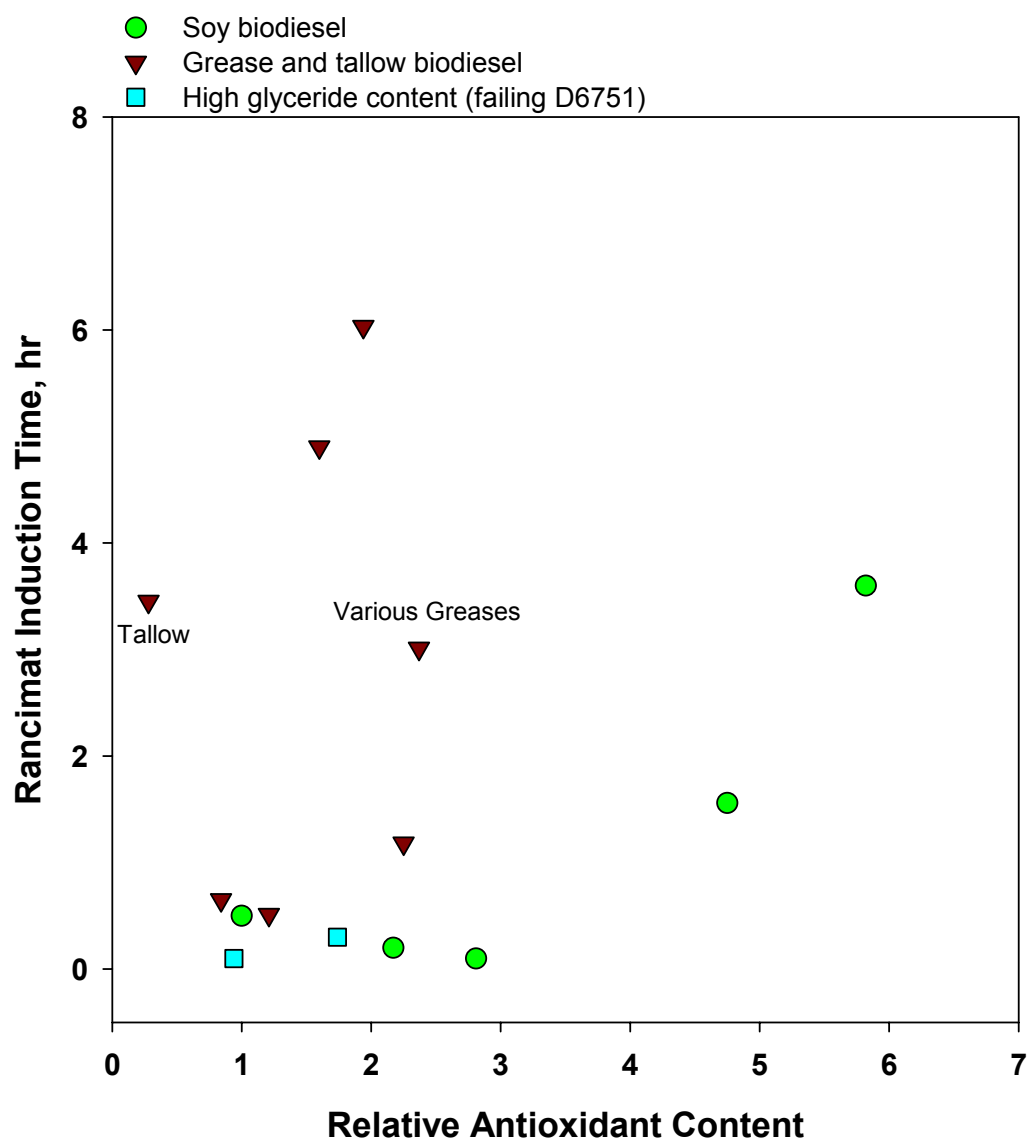


Figure 8. Relationship between relative antioxidant content and Rancimat induction time for different groups of biodiesel samples

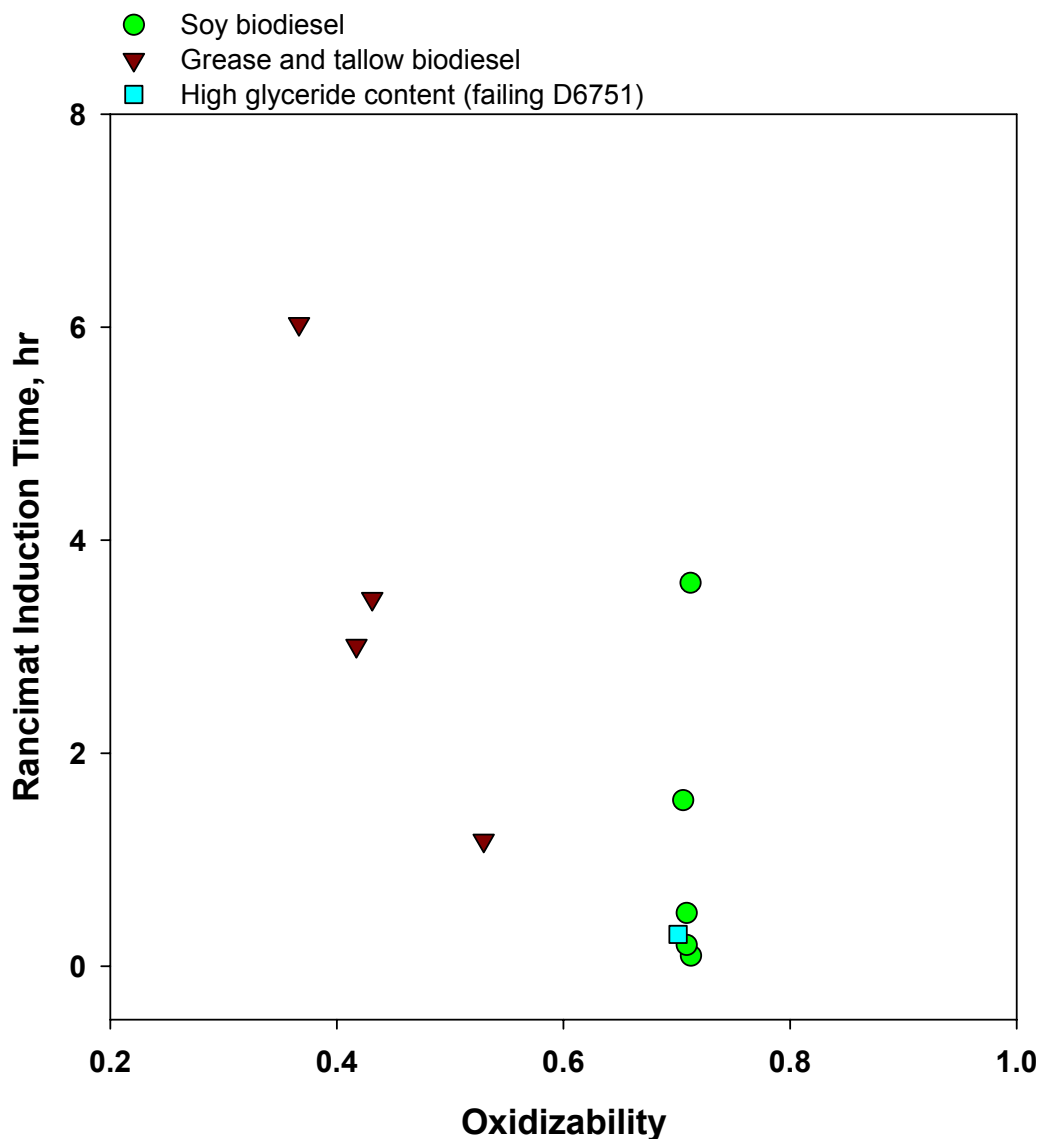


Figure 9. Relationship between oxidizability and Rancimat induction time for different groups of biodiesel samples

It is clear that additional research is required for a quantitative understanding of the factors that impact stability on these tests. However, for the samples examined here, the formation of insolubles on the D2274 test is measurably influenced by the antioxidant content, polyunsaturated content (or oxidizability), and the total glycerin content. The Rancimat induction time, on the other hand, appears to be mainly influenced by the oxidizability and to a lesser extent by the antioxidant content.

Thermal Stability Results

Gravimetric results for the D6468 test are shown in Figure 10, and a frequency distribution is shown in Figure 11. Values ranged from less than 1 mg/100 ml to over 25 mg/100 ml. For

petroleum diesel fuel, the standard test procedure measures filter reflectance rather than mass. The sediments that are formed in diesel fuel as a consequence of fuel instability in the D6468 test are generally dark. The sediments, when retained on a filter pad, do not reflect light nearly as well as the pad itself. Thus, with petroleum diesel fuel, there is a strong correlation between the decrease in reflectance and fuel instability. For the test conditions used here (150°C for 180 minutes) a minimum value of 70% reflectance is typically cited. The sediment that is formed during biodiesel instability reactions tends to not be as dark and coarse. Therefore these sediments tend to decrease reflectance to a lesser degree. The data associated with the D6468 test confirm this. The absolute values of the correlation coefficients associated with the amount of gravimetrically determine total insolubles to the reflectance, and the initial acid values were both less than 0.10.

Thermal Stability Discussion

It is difficult to interpret these results without some reference to gravimetric data on petroleum diesel fuels. Westbrook and Stavinoha [6, 9] have presented reflectance and gravimetric data for three petroleum diesel and three biodiesel samples. For this small dataset, petroleum fuels with less than 70% reflectance also produced approximately 10 mg/100 ml or more of filterable insolubles. The three biodiesel samples tested exhibited near 100% reflectance and filterable insoluble levels of 4 mg/100 ml or less. Earlier results presented by Lawrence [10], and shown here as Figure 12, confirm this approximate level. For the B100 samples examined here, 18 out of 27 produced filterable insolubles of 10 mg/100 ml or less, the remaining 9 samples were above this level. Several of Lawrence's biodiesel samples also exceeded this level.

Clearly additional work is required to fully quantify biodiesel thermal stability. While both the Southwest Research Institute (SwRI) and Magellan have implemented gravimetric versions of the D6468 test, it is not clear that both laboratories are performing insolubles measurements in the same way. Additionally, there are no data to allow an assessment of the precision of this modified test.

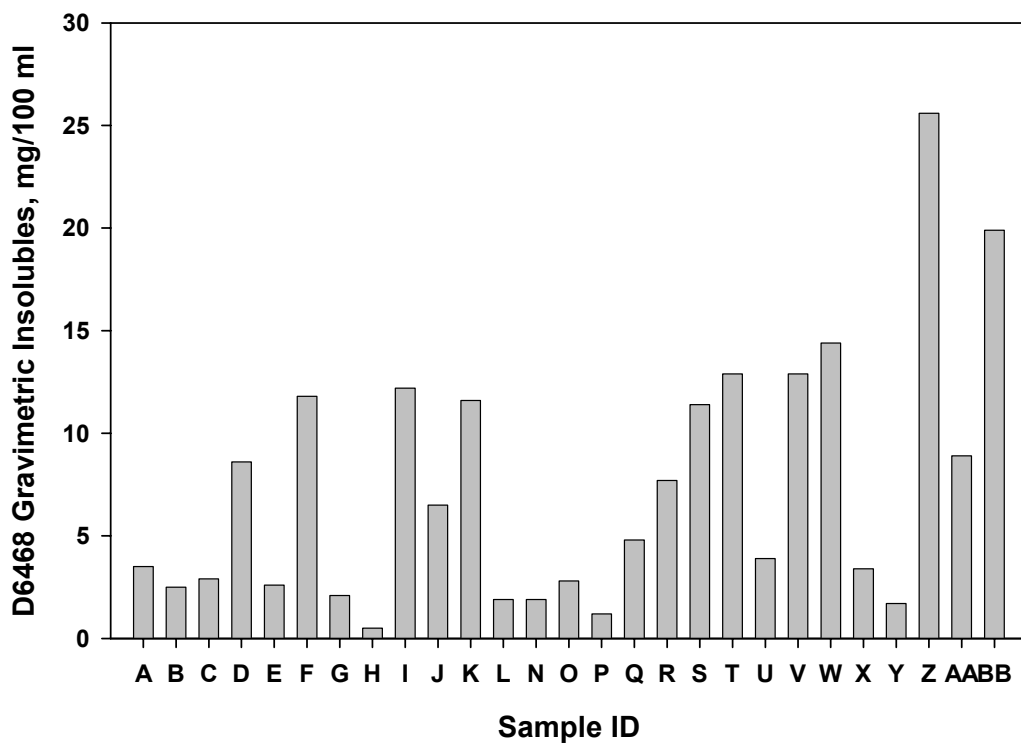


Figure 10. D6468 results for B100 quality survey samples

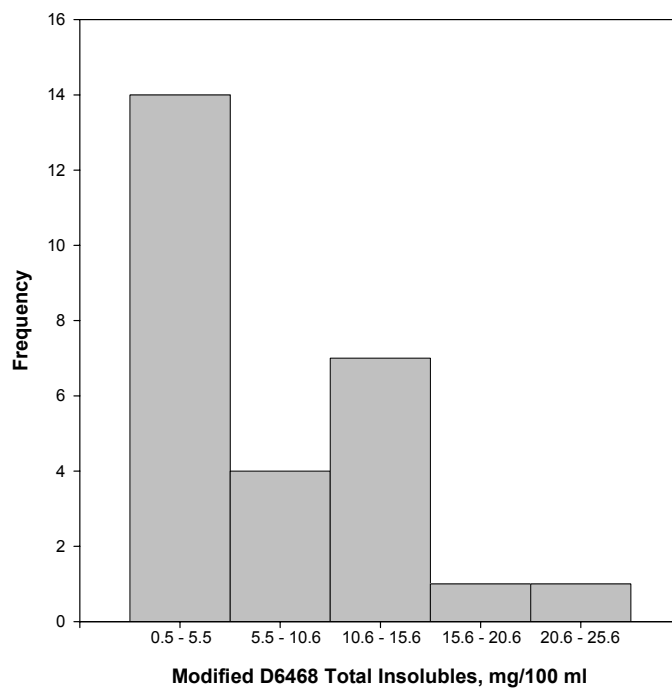


Figure 11. Frequency distribution for B100 Rancimat induction times

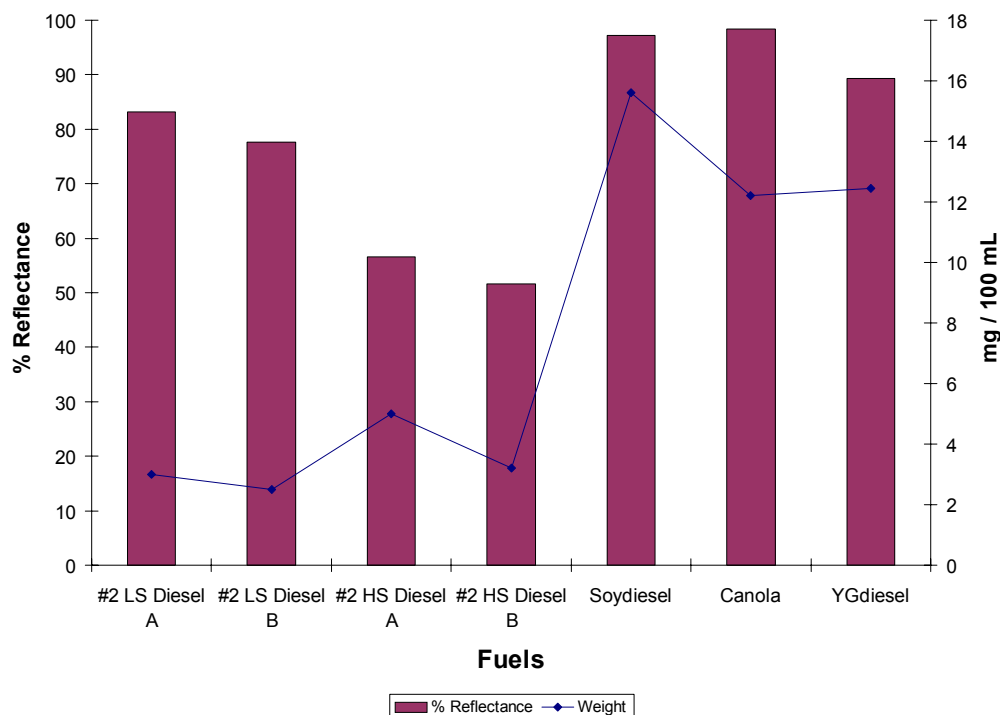


Figure 12. D5468 gravimetric and reflectance results for several diesel and B100 samples [10]

B100 Summary and Discussion

The phone surveys revealed that the distributors rely almost exclusively on the upstream party to deliver an on-specification, quality product. There is little recognition that problems can arise in the distribution chain. The data that comprise this survey tend to validate this approach. The off-specification conditions associated with these samples appear to stem from the production process. There was no evidence that any of the off-specification conditions or marginal results were the consequence of fuel handling practices. Given the lack of problems encountered by the distributors, the implementation of a formal quality control program will have to be driven by a demand from the downstream customers.

Of the 27 B100 samples, four (15%) did not comply with the standard specification for at least one fuel parameter. One sample was off-specification in terms of phosphorus, two for Total Glycerin, and two for Acid Number. Of the four off-specification samples, one was off-specification to the extent that immediate performance problems would probably result, depending on the concentration of biodiesel in the final blend. The other three off-specification samples would probably cause problems if a vehicle were to operate on the fuel over an extended period of time.

The ASTM specification for diesel fuel, D975, identifies five grades of fuel. From the point of production to the retail outlet, the fuel is identified as one of these five grades. None of the survey participants identified the biodiesel they handle or the sample that was submitted as being one of the two grades found in the ASTM specification for biodiesel. Two of the samples of biodiesel

had sulfur concentrations greater than 15 ppm, the maximum allowable level for S15 grade. However, since the fuel was not identified as either S15 or S500, it is not possible to determine if the samples meet the specification.

In Table 5, data points that are outliers for each parameter are identified. The outliers were determined using the Grubbs' test at a significance level of 0.05. In all cases, an outlier data point was accompanied by another outlier data point or an off-specification condition for that sample. Of the four samples that had an off-specification condition, three had an outlier data point for a different parameter, which was not an off-specification condition. In other words, it is rare for a sample to have only one abnormal condition.

Analysis of the B100 samples for Na and K indicates that the biodiesel has low levels of these contaminants in almost all cases. Analysis for Mg and Ca also generally shows low levels, however, there are several samples with more than 5 ppm of these metals. We speculate that the high levels of Mg and Ca mostly likely resulted from the use of hard water for washing.

The surveys of B100 stability show that a typical biodiesel has a short Rancimat induction time of less than one hour, and generates roughly 5 mg/100 ml of total insolubles in the D2274 accelerated stability test. However, a broad range of stability is indicated by the results with several samples showing much higher stability than typical. Additional research will be required to understand the implication of these results for inclusion of a stability requirement in ASTM D6751. The main factors affecting insoluble formation were antioxidant content, polyunsaturated content, and total glycerin content. The main factors affecting induction time were polyunsaturated content and antioxidant content.

Neither of the two storage stability methods had a significant correlation to the thermal stability method (D6468). The correlation coefficients for the D6468 and Rancimat data, and the D6468 and D2274 data were -0.14 and -0.03 respectively. Even though D6468 is a test for thermal stability and the other methods focus on storage stability, in petroleum diesel fuel there is some correlation associated with the methods. Results of the gravimetric thermal stability test for the biodiesels showed a wide range of results. Based on limited data, several of these samples may have produced levels of insolubles high enough for them to be classified as unstable. However, because this test is probably most meaningful as a predictor of what will happen to a finished fuel in the high temperature environment of an engine's fuel system, and because B100 samples will be used primarily as blending components rather than finished fuels, it is difficult to interpret these results.

Table 5. Identification of Outliers via Grubb's Test

Sample ID	D445 Kinematic Viscosity @ 40 °C (cSt)	D874 Sulfated Ash (% mass)	D5453 Sulfur (% mass)	D613 Cetane Number	D2500 Cloud Point (°C)	D524b Carbon Residue (% mass)	D664 Acid Number (mg KOH/g)	D6584 Free Glycerin (% mass)	D6584 Total Glycerin (% mass)	D4951 Phosphorus Content (% mass)
Specs	1.9 - 6.0	0.020	.0015 & .05	47	Report	0.05	0.8	0.02	0.24	0.001
A	4.489	0.000	0.00029	54.7	2	<0.010	0.25	0.003	0.208	0.0006
B	4.128	0.000	0.00036	49.6	0	<0.010	0.60	0.002	0.202	0.0008
C	4.085	0.005	0.00003	53.7	-2	<0.010	0.33	0.003	0.147	0.0005
D	4.361	0.015	0.00827	57.7	-1	0.015	0.24	0.004	0.239	0.0030
E	4.153	0.003	0.00268	53.7	-1	<0.010	0.59	0.003	0.190	0.0007
F	3.976	0.003	0.00134	58.3	-1	<0.010	0.11	0.012	0.019	0.0007
G	4.784	0.001	0.00012	48.0	-1	0.015	0.16	0.014	1.227	0.0005
H	3.991	0.000	0.00026	57.2	-1	<0.010	0.05	0.004	0.032	0.0005
I	4.099	0.000	0.00003	54.3	-1	<0.010	0.97	0.006	0.023	0.0002
J	4.145	0.000	0.00069	54.4	0	<0.010	0.35	0.004	0.171	0.0003
K	4.245	0.003	0.00115	51.9	0	0.018	0.76	0.003	0.192	0.0006
L	3.970	0.000	0.00032	54.7	-1	<0.010	0.05	0.004	0.037	0.0010
N	4.159	0.000	0.00105	48.8	0	<0.010	0.48	0.004	0.211	0.0008
O	4.093	0.001	0.00012	51.5	1	<0.010	0.70	0.003	0.198	0.0010
P	3.927	0.000	0.00005	55.1	-2	<0.010	0.03	0.002	0.011	0.0003
Q	4.107	0.003	0.00010	54.0	0	<0.010	0.34	0.008	0.067	0.0013
R	4.010	0.003	0.00035	56.4	-1	<0.010	0.02	0.002	0.013	0.0002
S	3.928	0.005	0.00089	56.1	-1	<0.010	0.02	0.006	0.020	0.0004
T	4.560	0.011	0.00145	56.3	2	0.043	1.38	0.018	0.317	0.0000
U	4.122	0.001	0.00006	57.6	-1	<0.010	0.65	0.004	0.195	0.0002
V	4.800	0.000	0.00127	54.2	5	<0.010	0.42	0.009	0.187	0.0000
W	4.134	0.000	0.00044	52.3	-1	<0.010	0.48	0.005	0.025	0.0001
X	4.100	0.002	0.00089	52.7	-2	<0.010	0.54	0.011	0.196	0.0002
Y	4.706	0.000	0.00081	65.0	14	<0.010	0.48	0.006	0.058	0.0004
Z	4.123	0.001	0.00014	53.3	-2	<0.010	0.34	0.001	0.022	0.0007
AA	4.610	0.000	0.00048	56.0	8	<0.010	0.52	0.005	0.102	0.0000
BB	4.087	0.001	0.00067	54.8	-1	0.013	0.35	0.014	0.025	0.0006
Outliers but not off-spec			Outliers and off-spec		Off-spec	Marginal result		Outliers and not S15		

B20 Fuel Quality Survey

Methods

Fifty fleets using B20 from across the country were selected to participate in the B20 quality survey. The basis of selection was two-fold: to represent the range of weather-related operating environments across the United States, and to represent all of the U.S. major (greater than 1 million gallons annual production) biodiesel producers. However, samples were collected in August and September of 2004 so the survey does not reveal properties relevant to wintertime operation.

The test plan consisted of tests or properties to be measured for the B20 samples, as shown below in Table 6. Magellan Midstream Partners performed all tests except oxidation stability by Rancimat. Robert Bosch Corporation and SwRI supplied replicate Rancimat data sets. In addition, Parker-Racor supplied interfacial tension measurements. The National Biodiesel Board's (NBB) B20 Fleet Evaluation Team, a committee of primarily automotive industry technical experts, proposed this list of tests.

Table 6. Tests Conducted for B20 Samples

Property	Test Method
Water and Sediment ^a	ASTM D2709
Visual Appearance	ASTM D4176 Procedure 2
Acid Number	WLS-102 (Field Acid Number)
Kinematic Viscosity	ASTM D445
Silver Strip Test	IP227
Peroxide Number	ASTM D3703
Oxidation Stability	EN14112 (Rancimat)
Water Extraction	GM Test Method
Density	ASTM D4062
Carbon Residue	ASTM D524
Biodiesel Content	FTIR Method
Cloud Point	ASTM D2500
Distillation (T90)	ASTM D86
Sulfur Content	ASTM D5453 or D2622, as appropriate

^aTest to be conducted only if D4176 haze rating is significant.

Results

All test results are listed in Appendix E. Results for the following tests showed no reason for concern (i.e., meeting D975 requirements for No. 2 diesel or otherwise within normal range): Water and Sediment, Visual Appearance, Kinematic Viscosity, Silver Strip Corrosion, Density, and Carbon Residue. The results for the balance of the tests conducted are discussed in more detail below.

Biodiesel Content

Figure 13 shows results of biodiesel content determination for the 50 B20 quality survey samples. Thirty-two of the samples were nominally B20 (between 18 and 22 percent biodiesel), while the remaining 18 samples exhibited biodiesel content from 7% to 98%. We believe that this indicates a serious issue with biodiesel blending practices. However, it should be noted that no specific protocol was followed for the collection of these samples. Most blenders prepare blends by so-called splash blending, where the blends are prepared by pumping biodiesel and petroleum diesel sequentially into a tank (typically a transport truck or storage tank). Apparently in many cases a homogeneous mixture of biodiesel and petroleum diesel is not being obtained. Because B100 is slightly more dense than petroleum diesel, a poorly blended tank will have a high biodiesel content on the bottom of the tank and a low biodiesel content at the top of the tank.

While the use of blends containing less than 20% biodiesel is not a concern from a maintenance and durability standpoint, the use of blends with dramatically high biodiesel content can cause serious issues. The NBB is currently working with biodiesel producers and blenders to make sure that proper blending procedures are followed. These primarily involve insuring that adequate splashing or turbulence is occurring during splash blending. As the industry grows, a transition from splash blending to in-line blending should occur and will eliminate this problem.

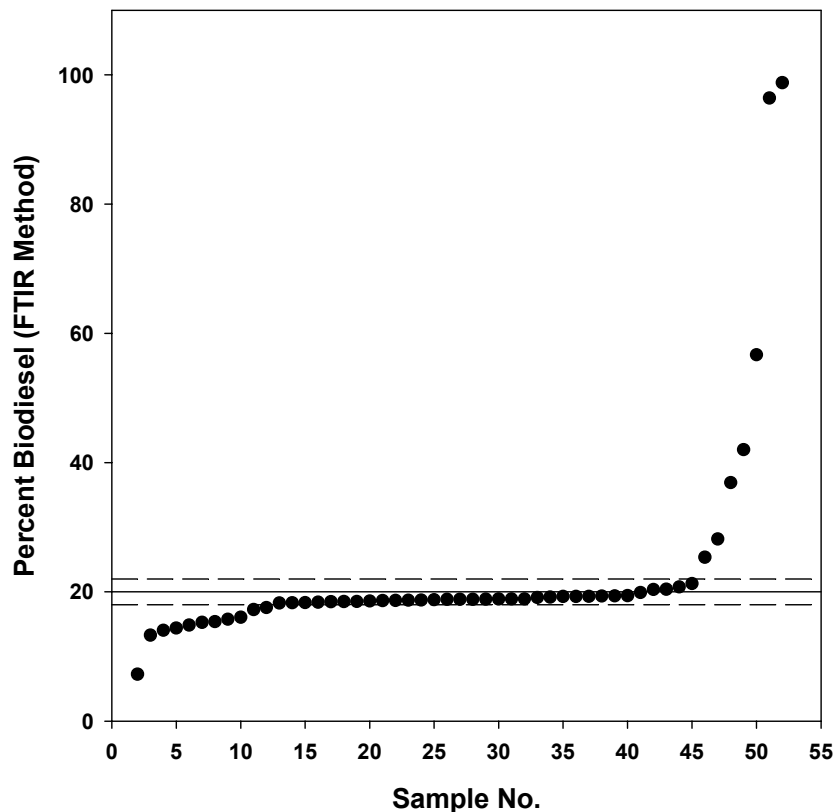


Figure 13. Percent biodiesel content for B20 quality survey samples

The range of acid numbers of the B20 samples is shown in Figure 14. Two samples exhibited high acid number (>0.6 mgKOH/g).



Figure 15 shows the range of cloud points encountered in the B20 samples. The cloud point of the B20 samples range from a low of -21°C (-6°F) to a high of 6°C (42°F). It must be noted that these samples were collected in September and October of 2004, prior to the beginning of the winter fuel season in most of the country. Thus the observed cloud point results are primarily for summertime fuels where cloud point is not significantly limited, but the geographic location of the samples may also influence the cloud point of the blends. The ASTM diesel fuel specification (D975) does not contain a cloud point specification; the cloud point is reported. Fuel manufacturers adjust the cloud point of the fuel to ensure consistent product quality on a market-by-market basis.

Figure 16 shows 90% recovery distillation temperatures for the survey samples. Many of the B20 samples meet the 338°C (640°F) upper limit for No. 2 diesel fuel, but a significant fraction does not. This suggests that any future B20 quality specification will require a slightly higher T90 limit than is currently used for No. 2 diesel.

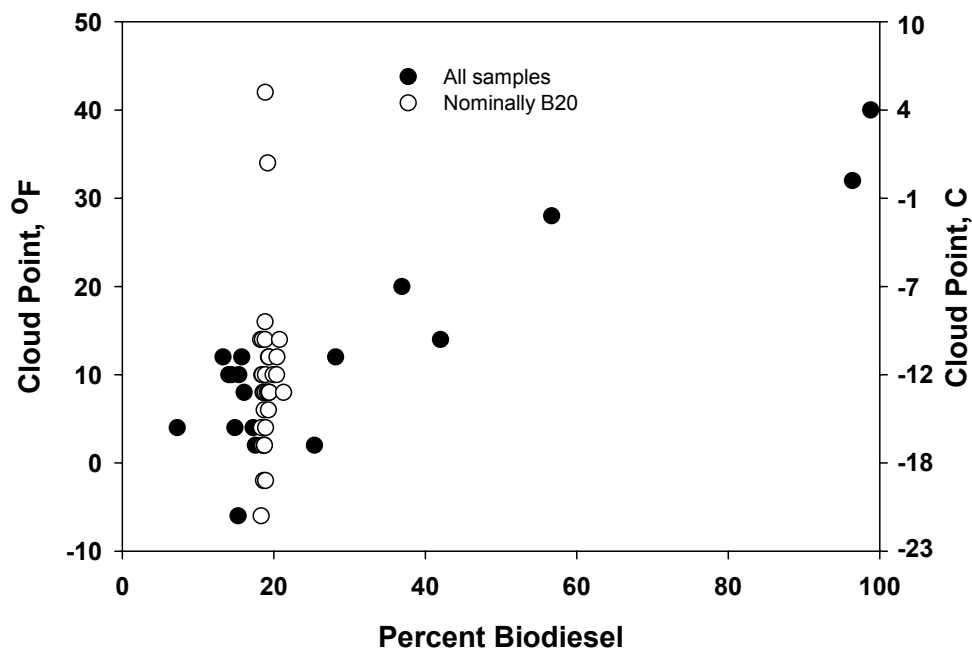


Figure 15. Cloud point (ASTM D2500) as a function of biodiesel content for B20 survey samples

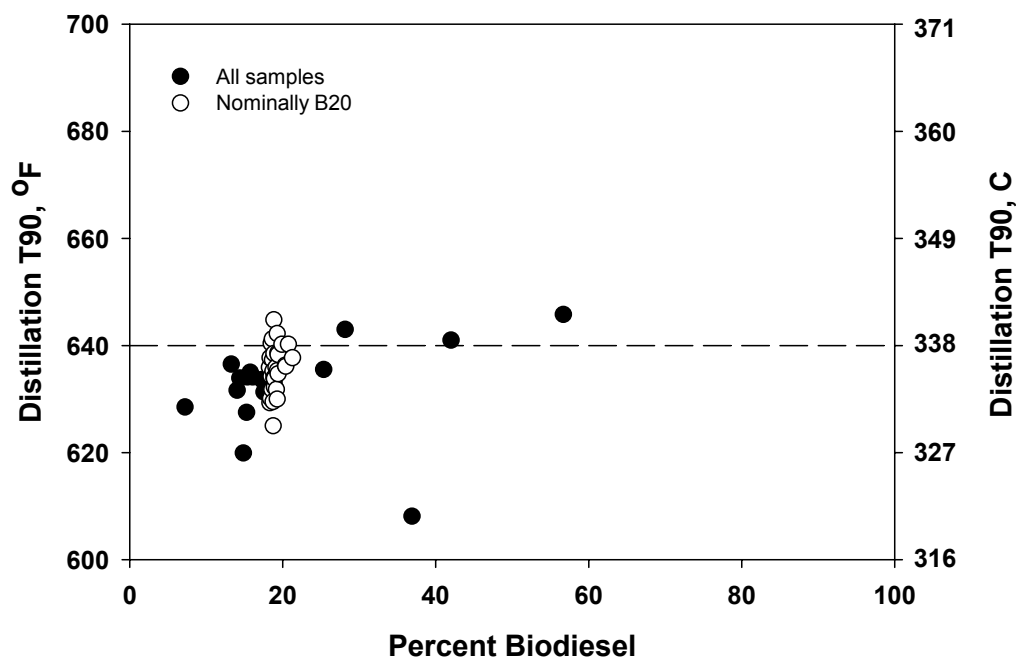


Figure 16. Distillation results (ASTM D86) for B20 quality survey samples
(horizontal dashed line shows upper T90 limit for No. 2 diesel fuel).

Peroxide Value

Figure 17 shows results of peroxide value measurements for the quality survey samples. Peroxides can form as a result of biodiesel or petroleum diesel oxidation, and ultimately

can decompose yielding aldehydes, acids, and polymers. Thus peroxides are intermediates in the fuel oxidation process. They are of concern because of the potential to form acids and deposits, and also because certain fuel system plastics and elastomers may degrade in the presence of certain types of peroxides. The results show a broad range of peroxide content from values less than 10 and are not of concern to values of several hundred.

While these high-peroxide values may raise significant issues, there are a number of unanswered questions that must be answered in order to understand their significance. First, we do not know the peroxide content of a typical diesel fuel, nor do we know the tolerance of diesel fuel system elastomers/plastics for diesel fuel derived peroxides. Second, this method for measuring peroxides was not developed specifically for biodiesel or biodiesel blends but for testing of gasoline and jet fuel. Thus it is possible that the reported high-peroxide values are an experimental artifact of applying this method to a substance for which it was not intended, and that peroxide levels are not, in fact, this high. Research to answer these questions is currently ongoing. Additionally, in the near future, the B100 quality specification will be modified to include an oxidation stability requirement. This will presumably prevent or limit the potential for peroxide formation.

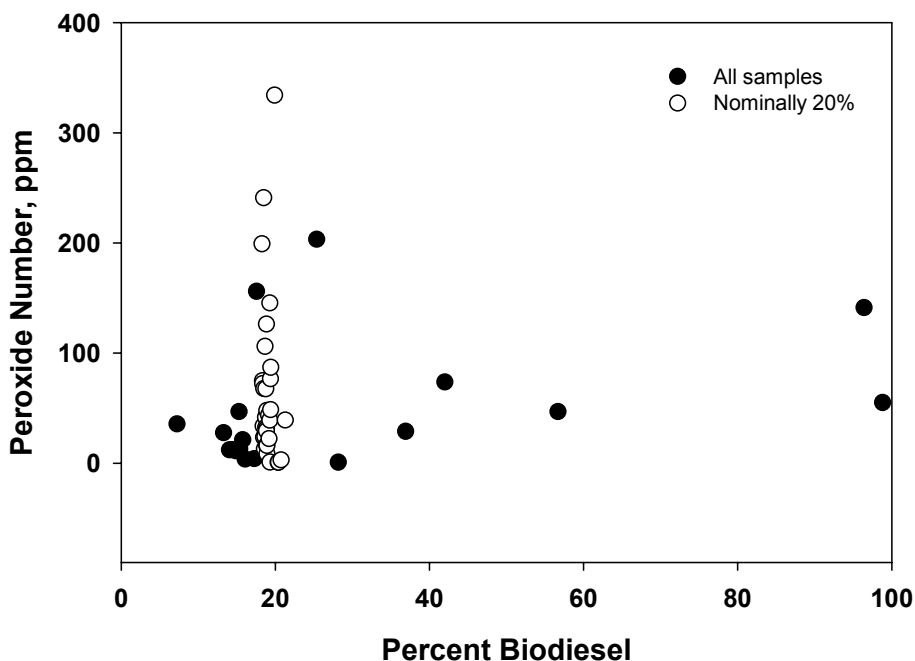


Figure 17. Peroxide value (or number) determined by ASTM D3703 for quality survey samples

Interfacial Tension

Parker-Racor kindly supplied the results for interfacial tension. These tests were conducted using ASTM D971 Interfacial Tension of Oil Against Water by the Ring Method. Results of water interfacial tension (IFT) measurements are shown in Figure 18. Having an adequately high IFT is required for on-board vehicle water separators that operate based on coalescence. A coalescer that operates in the upper 95% efficiency

range in high IFT fuel (around 30 dynes/cm) may drop up to 30% efficiency as the IFT decreases below 25 dynes/cm depending on the type of medium being used in the coalescer (per SAE J1488). So, coalescence as a mechanism for water separators (which most water separators depend on) is highly influenced by fuel chemistry (i.e., IFT).

Of the 33 samples analyzed, only six displayed IFTs above 15 dynes/cm. There were 13 samples that had IFTs at or below 10 dynes/cm. Of the six samples that had IFTs over 15 dynes/cm, the highest was only 19.5 dynes/cm. Water separation from diesel begins to become unpredictable below 25 dynes/cm. In areas where there is not much water in fuel, it would probably not be noticed. In areas where there is often water in diesel fuel, this could lead to higher injector maintenance costs, over long periods of time, than previously experienced using diesel fuels with higher IFT.

Thus, these results are a serious concern, but there are a number of outstanding questions. It is possible that the low IFT is caused by highly polar compounds in the biodiesel blends such as the peroxides noted above. Implementation of an oxidation stability requirement would in this case be expected to mitigate the problem of low IFT as well. Also, it is possible that other types of coalescer media and other types of water removal devices could be implemented. This might include the installation of specifically designed water separation filters/devices at the fuel dispenser nozzle for separation of water prior to pumping into the vehicle fuel tank.

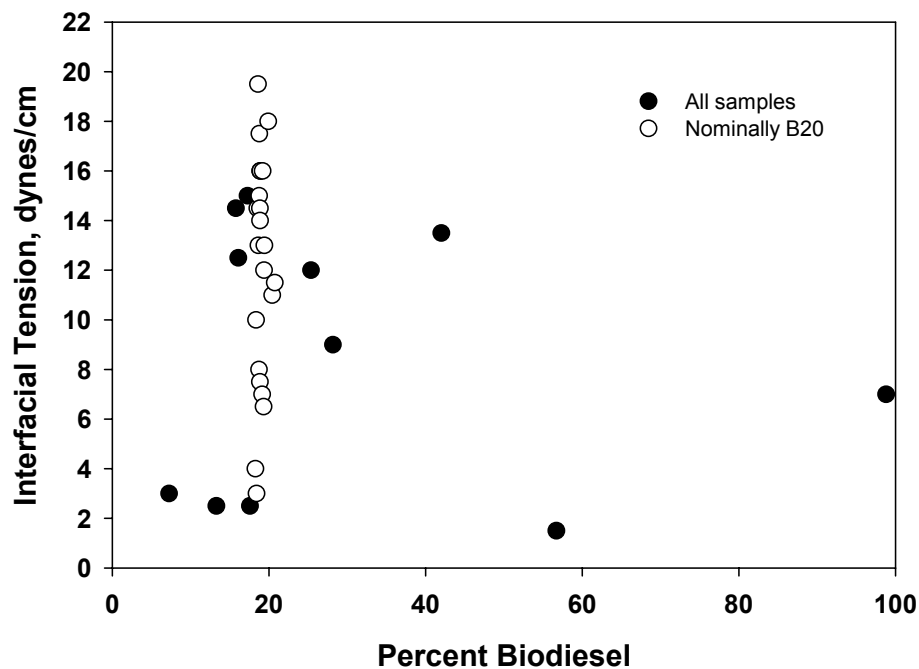


Figure 18. Results of water interfacial tension measurements by ASTM D971 for B20 survey samples

GM Water Extraction Test

The General Motors' (GM) water extraction test is an indirect way of measuring potentially corrosive species such as salts, acids, and bases left over from the esterification process. In this test, a 400 mL fuel sample is contacted with 40 mL of water. The conductivity and pH of the recovered water are measured, as is the amount of water recovered. In general, the pH results from this test do not raise any concerns. The water recovered varied considerably, with some tests showing that the B20 had dissolved as much as 6 volume percent water. This result seems questionable; it is highly unlikely that a B20 can hold this amount of water in solution. Figure 19 shows results for water conductivity, which varied over a wide range. There is some evidence to suggest that high-conductivity values correlate with high-peroxide content, as also shown in Figure 19. Thus if high-water conductivity is pointing to some fuel quality issue, it may be oxidation stability.

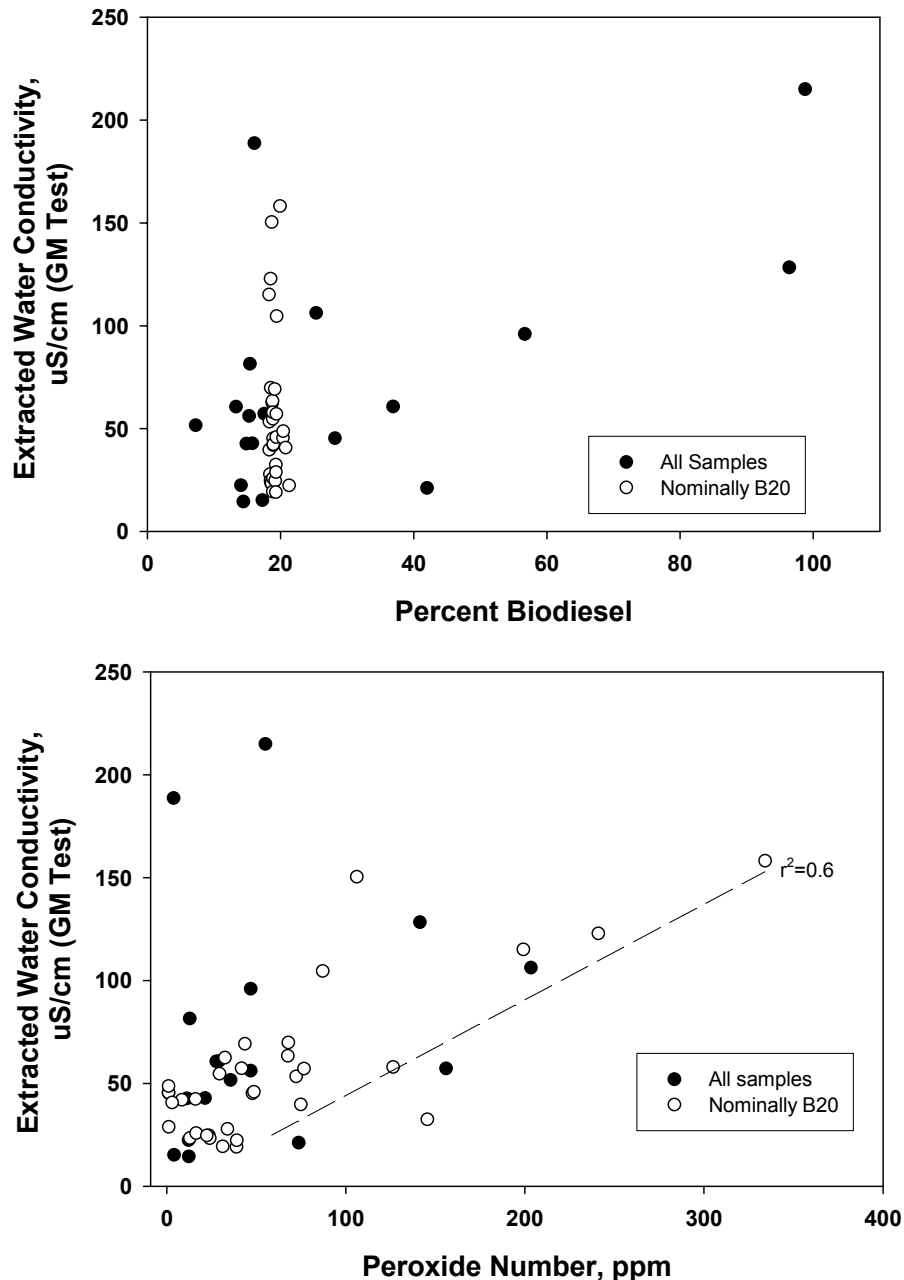


Figure 19. Conductivity results from the GM water extraction test as a function of percent biodiesel (top) and peroxide content (bottom)

Oxidation Stability by Rancimat

SwRI and the Robert Bosch Corporation kindly supplied the Rancimat test results. Detailed results are presented in Appendix F and are summarized in graphical form here. SwRI provided 20 replicate results for a peanut oil standard showing a mean of 5.04 hr, standard deviation of 0.22 hr, and 95% confidence interval of +/-0.1 hr. Figure 20 compares the average SwRI results (3 replications in most cases) and the Bosch results (single test). Results for the two labs correlate well, with a correlation coefficient of

0.84. However, there is a bias towards longer induction times for the samples tested at Bosch. Bosch indicated some issues with temperature calibration, and these results suggest that temperature was slightly low in their tests. Note that SwRI ended the experiment at 24 hours for three samples with very long induction times.

A striking feature of these results is evident from the frequency plot of Figure 21. Twenty-one out of the 36 samples tested exhibited induction times of less than 2.5 hr. Much longer induction times were anticipated based on the very long times typically reported for petroleum-derived diesel fuel, which makes up a large fraction of the composition of these samples. The short induction times may have been observed because of the age of these samples when tested. The samples were collected in September and October of 2004, and most analyses were conducted soon after. However, the Rancimat measurements were made in March and April of 2005, roughly 6 months later. Although these small samples were stored in an air-conditioned laboratory environment in sealed containers, the “oxidation reserve” of these samples may have been depleted during this time. It is recommended that for future quality surveys all tests should be conducted within one month of sample collection.

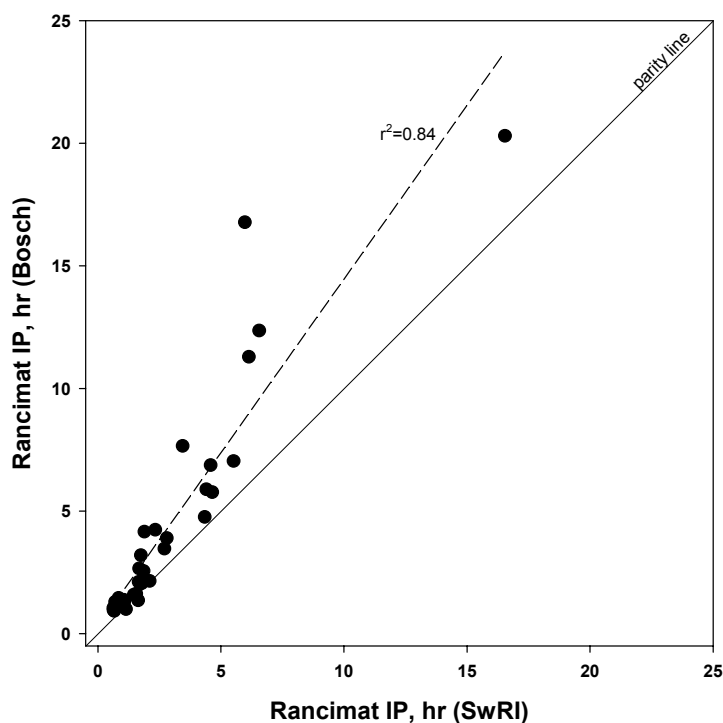


Figure 20. Comparison of B20 Rancimat oxidation stability test results from SwRI and Bosch

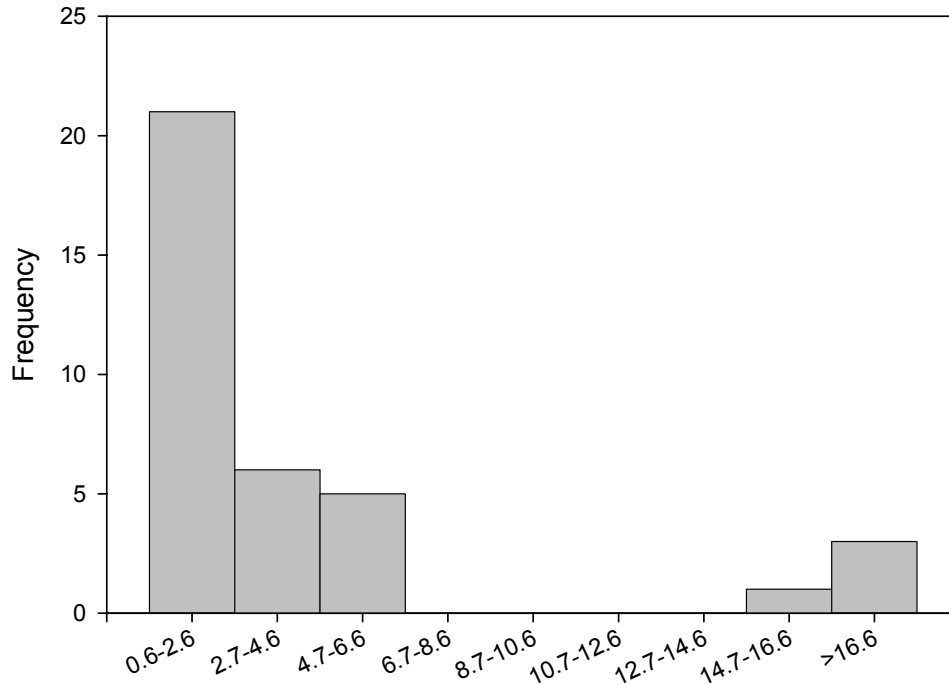


Figure 21. Frequency distribution for B20 Rancimat stability test results (SwRI data)

B20 Summary and Discussion

Because no fuel quality specification currently exists for B20, we cannot compare the results of this survey to standard requirements. Most of the properties examined showed acceptable levels for use in diesel engines. However, the survey data point to a number of issues and potential issues. Chief among these is the biodiesel content of the supposedly B20 samples. Only 32 out of the 50 samples contained nominally 20% biodiesel. The cause of this is believed to be inadequate mixing during splash blending of these fuels. This result is being made widely known to the biodiesel industry in hopes that education on proper blending procedures can solve this problem.

Additionally, many of the B20 samples exhibited high levels of peroxides. This is of concern because certain vehicle fuel system components are made of materials that may not be compatible with peroxides. However, this contention is based on experience with gasoline, and the peroxides that form in biodiesel are chemically much different having a much higher molecular weight. It is not known if biodiesel peroxides will produce the same effects on fuel system materials. Furthermore, it is widely agreed that the B100 specification, and perhaps the B20 specification, should include an oxidation stability requirement. Should such a requirement be implemented it seems highly likely that antioxidant additives would be used to meet it resulting in much lower potential for peroxide formation.

The B20 samples exhibited low IFT with water when tested using the ring method. A minimum level of IFT is required for the proper performance of water separators that are

used in engine fuel systems to protect the engine from water in the fuel. There are a number of potential causes of this problem, including the presence of highly polar materials such as peroxides in the biodiesel. Thus, this is another issue that might be resolved by implementation of an oxidation stability requirement.

The B20 samples were tested for oxidation stability by the Rancimat method. Many of the samples exhibited induction times of less than 2 hours, however, the samples had been stored for on the order of 6 months prior to the oxidation stability measurements. Thus it is not clear if the short induction times are intrinsic properties of these samples or are caused by the relatively long storage time where the samples capacity to resist oxidation was consumed.

Future surveys of B20 quality should ensure that all tests are conducted within one month of sample collection. Additionally, future surveys should include other oxidation stability tests such as ASTM D2274.

Conclusions and Recommendations

Based on the results of the B100 and B20 quality surveys conducted in 2004 the following conclusions were drawn:

- Biodiesel blenders and distributors rely almost entirely on the biodiesel manufacturer to ensure fuel quality. Little or no downstream product testing is conducted.
- The B100 samples included 4 produced from waste oils, 1 produced from tallow, and the balance produced from soy.
- Of the B100 samples collected, 85% met all of the requirements of ASTM D6751.
- Samples failing one requirement generally exhibited outlier or failing results for a second requirement.
- Distributors were not, at the time of this survey, distinguishing between S15 (15 ppm sulfur maximum) and S500 (500 ppm sulfur maximum) grades of biodiesel.
- Nearly all of the B100 samples exhibited Na+K and Mg+Ca levels below 5 ppm, a level thought to be acceptable for protection of fuel injection equipment.
- A typical U.S. biodiesel exhibits 5 mg/100 ml of deposits on the ASTM D2274 accelerated stability test and less than 1 hour induction time on the EN14112 Rancimat oxidation stability test. There is currently no oxidation stability specification for diesel fuels in the United States.
- The main factors affecting the stability of B100 are natural antioxidant content, polyunsaturated fatty ester content, and the presence of high levels of mono and diglycerides.
- An issue with splash blending of B20 blends was identified when it was discovered that 18 out of the 50 samples collected were not nominally B20. It is believed that insufficient turbulence or splashing occurred during the preparation of these blends.
- B20 samples showed high levels of peroxides, reinforcing the need for an oxidation stability requirement for B100 and perhaps for B20. While peroxide levels were not measured for B100, the formation of peroxides is well known as the initial step in fuel oxidation.
- The B20 samples exhibited low levels of water IFT, indicating that water separators on engine fuel systems will not perform as intended. The high peroxide levels may contribute to the low IFT.
- A typical B20 showed a less than 2 hour Rancimat (EN14112) induction time, but this may have been caused by storing the samples for 6 months prior to testing.

The following are recommendations based on the results of this study:

- Additional B100 and B20 surveys should be conducted on an ongoing basis to monitor the progress of the industry in meeting fuel quality requirements.
- A future B20 survey should be conducted in winter to allow an assessment of the impact of biodiesel blending on low-temperature properties.
- For future studies it is important that all analyses be performed within one month of sample collection, especially oxidation stability.
- Understanding of oxidation stability issues would be greatly enhanced by collection of field samples that have undergone significant oxidation.

Appendix A: Mono, Di, and Tri-Glyceride Content of B100 Samples

For calculation of total glycerin in ASTM D 6584, the following equation is used:

$$\text{total glycerin} = \text{free glycerin} + \text{bound glycerin} \quad (1)$$

where:

$$\begin{aligned} \text{bound glycerin} &= \Sigma (Gl_M, Gl_D, Gl_T) \\ Gl_M &= 0.2591 \Sigma (\text{monoglyceride, mass \%}) \\ Gl_D &= 0.1488 \Sigma (\text{diglyceride, mass \%}) \\ Gl_T &= 0.1044 \Sigma (\text{triglyceride, mass \%}) \end{aligned}$$

While Table 7 shows total glycerin reported as mass percent (mass%) glycerin, the test method requires measurement of the actual glyceride content. It is instructive to examine these numbers, and they are shown in the table below. Samples failing or marginal for the total glycerin requirement all exhibit relatively high levels of unconverted triglycerides. Triglycerides, or fat, have an extremely high boiling point relative to biodiesel or diesel fuel and can lead to the formation of fuel injector tip and other combustion chamber deposits. The total amount of unconverted or partially converted material in the sample can also be quite high. Sample G exhibits a total glycerin five times the allowable level of 0.24 wt% and actually contains more than 7 weight percent of unconverted or partially converted material (i.e. this sample is less than 93% biodiesel). Sample D is right at the allowable limit and contains slightly more than 1% unconverted or partially converted material.

Table 7. Mono, Di, and Tri-Glyceride Content of B100 Samples

	Free Glycerine	Total Glycerin	Monoglyceride	Diglyceride	Triglyceride
Sample	% mass	% mass	% mass	% mass	% mass
A	0.003	0.208	0.624	0.213	0.107
B	0.002	0.202	0.633	0.166	0.109
C	0.003	0.147	0.475	0.124	0.027
D	0.004	0.239	0.597	0.374	0.239
E	0.003	0.19	0.630	0.143	0.025
F	0.012	0.019	0.028	0.000	0.000
G	0.014	1.227	1.837	2.802	3.066
H	0.004	0.032	0.093	0.027	0.000
I	0.006	0.023	0.059	0.009	0.000
J	0.004	0.171	0.563	0.127	0.016
K	0.003	0.192	0.601	0.168	0.075
L	0.004	0.037	0.106	0.030	0.005
N	0.004	0.211	0.596	0.213	0.198
O	0.003	0.198	0.667	0.135	0.017
P	0.002	0.011	0.035	0.000	0.000
Q	0.008	0.067	0.172	0.085	0.014
R	0.002	0.013	0.039	0.000	0.000
S	0.006	0.02	0.046	0.014	0.000
T	0.018	0.317	0.687	0.384	0.608
U	0.004	0.195	0.641	0.152	0.020
V	0.009	0.187	0.399	0.292	0.293
W	0.005	0.025	0.070	0.014	0.000
X	0.011	0.196	0.603	0.163	0.045
Y	0.006	0.058	0.196	0.009	0.000
Z	0.001	0.022	0.077	0.009	0.000
AA	0.005	0.102	0.357	0.030	0.000
BB	0.014	0.025	0.043	0.000	0.000

Appendix B: Results of B100 FAME Analysis

A subset of the biodiesel samples were analyzed by gas chromatography with mass spectrometric detection (GC-MS). The instrument used is a Hewlett-Packard HP6890 GC and includes electronic pressure control. The mass selective detector (MSD) is model HP5973 and the automatic liquid sampler is model HP7683. The GC was fitted with a Varian capillary column designed for FAME analysis: 100m x 250 μ m, 0.25 μ m film of 'CP Select'. Helium was the carrier gas at 1.5 mL/min (constant). The injected sample volume was 1 μ L, and an injection split ratio of 100:1 was used. The chromatography conditions were:

- Initial temp: 150°C for 6 minutes
- Ramp: 4°C/min
- Final temp: 250°C for 4 minutes
- Total run time: 35 minutes.

The MSD was operated in the electron impact ionization mode, scanning masses from 33-450 amu.

The biodiesel samples were all prepared gravimetrically (21-26mg) and then dissolved in 1.0mL of methanol. FAME standard mixtures from Alltech were prepared in the same manner and used to calibrate the GC-MS. These were American Oil Chemists Society mixtures 1, 3, 5, and 6. For some species there was only a single point calibration; others had two to four levels of concentration between the four standard mixtures. In the latter case, we had the choice of using an average response factor, or one that was based on the slope of a linear regression of the calibrations. The data reported in Table 8 are based on average response factors (or a single response factor when only one was available). All compounds used mass 74 for quantitation, except methyl linoleate and methyl linolenate, which used masses 67 and 79 respectively.

Detailed results are shown on the following pages.

Table 8. Results of FAME Analysis by GC-MS for B100 Samples

	Sample	A	B	F	G	H	K	N	O	R	U	V	Y	Z	AA
FAME	Name	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
C8:0	Methyl Caprylate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10:0	Methyl Caprate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12:0	Methyl Laurate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C14:0	Methyl Myristate	0.22	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.62	2.63	0.28	0.76
C16:0	Methyl Palmitate	12.26	9.37	9.45	9.39	9.36	9.41	9.34	9.33	9.37	9.37	15.86	26.39	8.44	17.26
C16:1	Methyl Palmitoleate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.99	2.75	0.00	1.26
C18:0	Methyl Stearate	5.70	3.55	3.86	3.61	3.84	3.55	3.50	3.56	3.92	3.80	9.11	19.99	4.60	11.86
C18:1	Methyl Oleate (9)	30.27	19.49	19.45	18.97	19.35	19.57	19.36	19.53	19.53	19.27	34.26	38.54	22.95	36.02
C18:1	Other Isomers														
C18:2	Methyl Linoleate (9,12)	47.69	57.35	57.68	58.00	58.41	57.30	57.46	57.33	57.54	57.62	35.32	8.92	60.06	29.97
C18:3	Methyl Linolenate (6,9,12)	3.28	9.85	9.36	9.63	8.77	9.76	9.97	9.85	9.46	9.51	3.41	0.66	3.32	2.42
C20:0	Methyl Arachidate	0.32	0.22	0.18	0.20	0.18	0.22	0.18	0.22	0.17	0.24	0.25	0.12	0.24	0.25
C22:0	Methyl Behenate	0.27	0.18	0.00	0.20	0.00	0.18	0.18	0.18	0.00	0.19	0.19	0.00	0.12	0.20
C22:1	Methyl Eurcate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C24:0	Methyl Lignocerate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mass Closure %	86.9	104.3	103.3	94.1	101.9	103.3	103.5	104.3	104.7	102.5	75.1	76.7	91.8	72.4

Appendix C: Procedure for Biodiesel Testing Using DPPH Redox Indicator

The procedure was a modification of a published method [3].

A $3.35 \cdot 10^{-4}$ M solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH, free radical purchased from Aldrich Chem. Co) in methanol (HPLC-grade, J.T. Baker) was prepared at room temperature. Then 3 mL of this standard solution was placed in a quartz cuvette, a 100 μ L sample of biodiesel was added, and the mixture was stirred vigorously for 1 min. The change in absorbance was measured using a UV-VIS apparatus (HP 8453) at a fixed $\lambda_{\text{max}} = 515$ nm over regular time intervals (1, 2, 3, 4, 5, 10, 15, 30, 60 min). A sample of pure DPPH/MeOH solution served as 'blank' to measure the absorbance at $t=0$ min. The change in absorbance for a randomly selected biodiesel sample (Sample R) was arbitrarily assigned a value of 1, and all other samples are referenced to this value for a relative antioxidant content.

Appendix D: Additional Modifications to the D2274 Test Method

In the fairly recent past, a number of test methods, which include filtration followed by weighing the filter media, have incorporated a “tare” or “blank” filter pad for control purposes. The inclusion of the blank filter pad allows changes in atmospheric conditions, most noticeably relative humidity, from contributing to overall test variability. This takes the form of placing a “blank” filter pad under the experimental pad during the course of the filtration procedure. The “blank” pad is dried and weighed in the same manner as the experimental pad. Once the weights are determined, the change in the weight of the “blank” pad is subtracted from the change in the weight of the experimental pad. The logic on which the inclusion of the “blank” pad is based is that the sediment material that has a greater diameter than the nominal pore size of the filter pad will be retained on the experimental pad, and the sediment that has a diameter less than the pore size will pass through both the experimental and “blank” pads.

This is similar to the inclusion of a “tare” beaker in the determination of adherent insolubles. This “tare” beaker is handled exactly like the experimental beakers, except no sample is introduced into the beaker. Again, once the weights are determined, the change in the weight of the “tare” beaker is subtracted from the change in the weight of the experimental beakers.

This similarity is not exact because the “tare” beaker is never exposed to any of the sample, and 100% of the oxidized sample goes through the “blank” filter pad. Therefore the only contribution to the “tare” beaker is the changes in atmospheric conditions, whereas the exposure of the “blank” pad to the sample provides an additional contributor to the change in weight of the pad. The exposure of the “blank” pad to biodiesel has a much greater impact on the change in weight of the pad than the changes in atmospheric conditions. This is due to the atypical characteristics of the sediment associated with biodiesel oxidation.

As a consequence of recognition that the “blank” pad was retaining additional sediment, and thus acting as a second experimental pad, the D2274 data was re-examined. Instead of subtracting the change in the weight of the “blank” pad, the change in weight was added to the increase in the weight of the experimental pad. The results from this re-examination appear in the following table.

Table 9. D2274 Data with the Control Pad Modification

D2274 Data w/ the Control Pad Modification

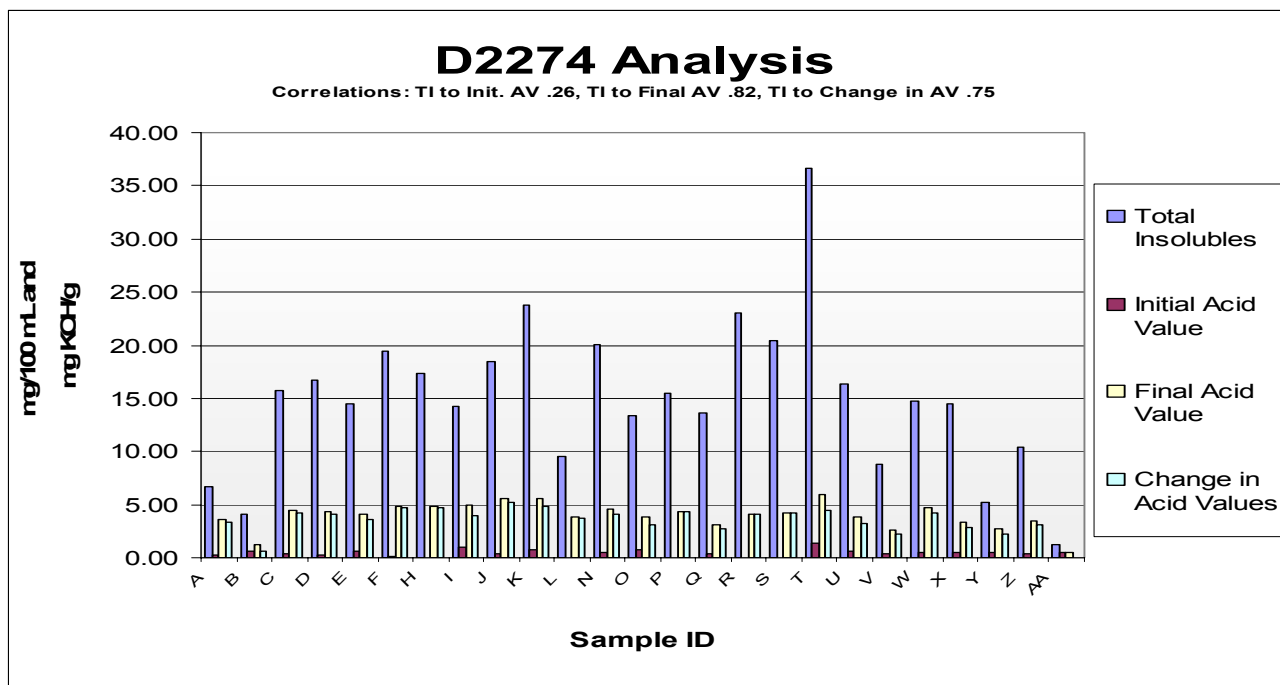
Data after Adjustments in Calculations										Original Data									
ASTM D2274 INSOLUBLES										ASTM D2274 INSOLUBLES									
Spl	Run ID	Filter.	Adher	Total	Ranges Divided by Averages			Filter Insol	Adher Insol	Total Insol	Filter.	Adher	Total	Ranges Divided by Averages			Filter Insol	Adher Insol	Total Insol
		mg/.1 L	mg/.1 L	mg/.1L	Filterable	Adherent	Total	Abs Range	Abs Range	Abs Range				mg/.1 L	mg/.1 L	mg/.1L	Filterable	Adherent	Total
A	1	5.09	0.71	5.80	28%	21%	27%	1.63	0.17	1.80	0.86	0.71	1.57	68%	21%	50%	0.89	0.17	1.06
	2	6.71	0.89	7.60							1.74	0.89	2.63						
	Avg	5.90	0.80	6.70							1.30	0.80	2.10						
B	1	2.54	0.54	3.09	32%	93%	47%	0.97	0.94	1.91	-0.03	0.54	0.51	300%	93%	104%	0.17	0.94	1.11
	2	3.51	1.49	5.00							0.14	1.49	1.63						
	Avg	3.03	1.01	4.04							0.06	1.01	1.07						
C	1	13.49	3.14	16.63	12%	8%	11%	1.57	0.23	1.80	1.83	3.14	4.97	47%	8%	16%	1.11	0.23	0.89
	2	11.91	2.91	14.83							2.94	2.91	5.86						
	Avg	12.70	3.03	15.73							2.39	3.03	5.41						
Z	1	8.37	2.14	10.51	5%	44%	3%	0.43	0.77	0.34	2.77	2.14	4.91	10%	44%	23%	0.26	0.77	1.03
	2	8.80	1.37	10.17							2.51	1.37	3.89						
	Avg	8.59	1.76	10.34							2.64	1.76	4.40						
AA	1	0.46	0.11	0.57	92%	136%	105%	0.77	0.49	1.26	0.06	0.11	0.17	86%	136%	125%	0.09	0.49	0.57
	2	1.23	0.60	1.83							0.14	0.60	0.74						
	Avg	0.84	0.36	1.20							0.10	0.36	0.46						
Averages for the entire sample set:																			
Averages (12.91	2.47	15.38	27%	28%	26%	3.03	0.54	3.31	2.46	2.47	4.93	54%	28%	32%	0.83	0.54	1.06

The most immediate impact associated with adding the increase in the weight of the “blank” pad is the significant increase in the filterable insolubles, the average weight increased from 2.46 to 12.91 mg/100mL. This modification had a significant impact on the precision of the test. The difference in the two filterable insolubles (the range of the values) as a percentage of the average result decreased from 54% to 27%. Of course, with the significant increase in the filterable insolubles, there was an associated increase in the range of results—an increase from 0.83 to 3.03 mg/100mL.

There was no change in the adherent insoluble test procedure or results, so this had a buffering impact on the changes in the filterable insolubles on the total insolubles results. The average increase in total insolubles increased from 4.93 to 15.38 mg/100mL. This translated to an improvement in the precision of the overall method, as measured by the range of the values as a percentage of the average value, of 6% (from 32% to 26%).

This improvement in precision did have an appreciable impact on how well the D2274 data correlated to acid values and the Rancimat data. The correlation coefficients for the unmodified D2274 results to the initial acid values, final acid values and the change in acid values were 0.13, 0.65, and 0.61, respectively. They improved to 0.25, 0.82 and 0.76 with the recalculated D2274 values. The correlation of the recalculated D2274 data to the Rancimat data improved from -0.66 to -0.72.

The original D2774 data did not correlate to the D6468 data, and that condition did not change; the correlation coefficient went from -0.03 to 0.01.



The logical conclusion arising from this improvement in how well the D2274 data correlates to the other stability indicators is that if the precision of the D2274 method can be further improved, there will be a corresponding improvement in the correlations. A cursory evaluation of the data from this perspective suggests that a significant opportunity for improvement exists. This conclusion is drawn from an examination of the variability of the amount of material that is retained on the control filter pad. If the amount of material retained on the control pad is consistently 40% of the total filterable insolubles (another way to say that is 67% of the weight of the experimental pad) then no opportunity for improvement exists. Even if it is known that a substantial amount of insolubles passes through both pads, if that amount is biased by a constant amount, then no significant improvement in the correlation will be achieved.

Both analysts' observations and the data indicate that significant improvement is achievable. The analysts have noted that during some of the filtrations of the oxidized biodiesel there is "goo" that passes through the pads and is observed in the filtrate. This is not observed in all cases. The increase in weight in the control pad as a percentage of the total filterable insolubles varied from 22% to 49% in this data set, with the average being 40%. If a dependable means by which the amount of this "filterable insolubles" can be quantified, the precision of the test would improve dramatically. At that point, the primary source of imprecision would be the ability of the test to generate a consistent amount of insolubles in the reaction phase of the test.

Appendix E: Detailed Results for B20 Survey

Sample ID	D2709 Water and Sediment (% vol)	D4176 Haze Rating	WLS 102 Field Acid Number	D445 Kinematic Viscosity@ 40°C (cSt)	MAS001 Silver Strip Test	D3703 Peroxide Number (ppm)	D524 Carbon Residue (% mass)	D5773 Cloud Point (°F)	GM EXT pH	GM EXT (μS/cm)	GM EXT Water Recovered (mL)	D4052 Density (g/mL@ 60°F)	D5453 Sulfur Content (ppm)	D2622 Sulfur Content (ppm)	Biodiesel Content (% vol)	D86 90% Recov
04070862	NA	1	0.08	2.749	0	35.6	<0.010	4	6.8	51.6	39	0.8571	302	N/A	7.25	628.5
04070863	NA	1	0.11	3.001	0	27.7	0.017	12	5.5	60.6	40	0.8587	272	N/A	13.29	636.5
04070864	NA	1	0.06	2.218	0	12.2	<0.010	10	7.2	22.4	37	0.8335	56	N/A	14.04	631.6
04070865	NA	1	0.14	2.739	0	12.3	0.022	10	7.3	14.5	31	0.8589	287	N/A	14.41	633.9
04070866	NA	1	0.11	2.838	0	11.3	0.017	4	6.1	42.7	28	0.8632	350	N/A	14.86	619.9
04070867	NA	1	0.11	2.966	0	46.9	0.021	-6	6.8	56.1	38	0.8497	217	N/A	15.28	627.5
04070868	NA	1	0.75	2.524	0	12.9	0.018	10	4.4	81.5	33	0.8473	34	N/A	15.39	634.1
04070869	NA	1	0.08	2.841	0	21.4	0.016	12	7.2	42.8	30	0.8534	266	N/A	15.77	635.0
04070870	NA	1	0.11	2.154	0	3.8	<0.010	8	5.0	189	38	0.8393	226	N/A	16.08	634.1
04070871	NA	1	0.03	2.731	0	4.1	0.018	4	6.9	15.2	33	0.8602	259	N/A	17.27	633.6
04070872	NA	1	0.03	2.774	0	156.0	0.033	2	6.9	57.2	20	0.8610	242	N/A	17.56	631.3
04070873	NA	1	0.17	2.697	0	199.1	<0.01	14	4.8	115	33	0.8464	90	N/A	18.27	635.9
04070874	NA	1	0.15	2.603	0	74.9	0.013	-6	5.7	39.7	37	0.8559	150	N/A	18.32	629.3
04070875	NA	1	0.08	3.330	0	72.3	0.041	4	5.1	53.3	17	0.8683	325	N/A	18.34	637.7
04070876	NA	1	0.06	2.838	0	33.9	<0.01	10	5.7	27.8	35	0.8593	258	N/A	18.40	630.1
04070877	NA	1	0.06	3.040	0	241.0	0.018	14	5.5	123	38	0.8621	245	N/A	18.48	737.4
04070878	Trace	4	0.14	2.739	0	23.5	0.030	2	5.4	24.7	15	0.8560	186	N/A	18.49	634.2
04070879	NA	1	0.06	2.979	0	67.9	0.016	10	4.6	69.8	30	0.8596	248	N/A	18.51	640.4
04070880	NA	1	0.06	2.59	0.00	13.0	<0.010	8	6.85	23.4	35	0.8523	155	N/A	18.59	631.8
04070881	NA	1	0.08	2.900	0	24.0	0.024	-2	6.7	23.3	34	0.8705	318	N/A	18.64	641.2
04070882	NA	1	0.08	2.745	0	106.1	0.016	8	5.3	150	39	0.8654	301	N/A	18.67	637.3
04070892	NA	1	0.06	2.684	0	41.8	<0.010	6	7.3	57.3	39	0.8531	239	N/A	18.72	635.2
04070893	NA	1	0.17	2.299	0	32.5	<0.010	2	6.4	62.5	38	0.8442	199	N/A	18.74	629.5
04070894	NA	1	0.11	2.857	0	67.6	<0.010	2	5.7	63.4	31	0.8650	201	N/A	18.77	625.0
04070895	NA	1	0.20	2.945	0	31.3	0.015	16	6.7	19.3	27	0.8542	298	N/A	18.84	644.8
04070897	NA	1	0.11	3.095	0	29.5	0.015	14	6.2	54.7	39	0.8610	199	N/A	18.85	638.5
04070898	NA	1	0.06	2.849	0	126.4	<0.01	8	5.1	57.9	40	0.8584	268	N/A	18.85	634.0

Sample ID	D2709 Water and Sediment (% vol)	D4176 Haze Rating	WLS 102 Field Acid Number	D445 Kinematic Viscosity@ 40°C (cSt)	MAS001 Silver Strip Test	D3703 Peroxide Number (ppm)	D524 Carbon Residue (% mass)	D5773 Cloud Point (°F)	GM EXT pH	GM EXT (µS/cm)	GM EXT Water Recovered (mL)	D4052 Density (g/mL@ 60°F)	D5453 Sulfur Content (ppm)	D2622 Sulfur Content (ppm)	Biodiesel Content (% vol)	D86 90% Recov
04070910	NA	1	0.11	3.629	0	16.4	<0.01	42	6.4	25.8	39	0.8359	155	N/A	18.86	--
04070911	NA	1	0.06	2.852	0	47.9	0.103	10	7.3	45.2	26	0.8572	218	N/A	18.88	632.9
04070912	NA	1	0.11	2.750	0	8.5	0.018	-2	6.9	42.0	33	0.8654	269	N/A	18.90	632.2
04070913	NA	1	0.14	2.161	0	16.1	<0.010	4	6.1	42.3	40	0.8366	214	N/A	18.91	633.8
04070914	NA	1	0.28	2.666	0	43.6	0.013	8	5.7	69.2	17	0.8570	266	N/A	19.13	635.9
04070915	NA	1	0.16	2.491	0	22.4	<0.010	34	6.9	24.6	34	0.8422	3	N/A	19.19	631.8
04070917	NA	1	0.06	2.547	0	39.0	<0.010	6	6.8	19.1	33	0.8424	3	N/A	19.28	630.0
04070918	NA	1	0.03	3.042	0	145.6	0.033	12	7.3	32.5	28	0.8688	293	N/A	19.29	642.2
04070919	NA	1	0.06	2.798	0	1.1	<0.010	8	7.4	28.8	35	0.8598	194	N/A	19.30	635.3
04070920	NA	1	0.06	3.080	0	76.7	0.016	12	6.6	57.1	33	0.8655	268	N/A	19.36	638.6
04070921	NA	1	0.11	2.713	0	48.7	<0.010	8	6.6	45.8	33	0.8487	45	N/A	19.38	638.3
04070922	NA	1	0.06	2.808	0	87.1	0.041	8	4.5	105	39	0.8610	258	N/A	19.41	634.7
04070923	NA	1	0.08	2.957	0	334.2	0.016	10	4.6	158	40	0.8572	262	N/A	19.91	640.2
04070960	NA	1	0.11	2.985	0	<1.0	<0.010	10	6.6	45.5	39	0.8637	200	N/A	20.36	636.3
04070961	NA	1	0.14	2.841	0	<1.0	0.021	12	5.9	48.7	30	0.8632	N/A	2868	20.40	636.1
04070963	NA	1	0.22	2.882	0	3.1	<0.01	14	7.6	40.7	26	0.8570	240	N/A	20.75	640.2
04071007	NA	1	0.19	2.883	0	39.1	0.031	8	6.0	22.3	39	0.8662	264	N/A	21.29	637.7
04071046	NA	1	0.06	2.474	0	203.4	<0.010	2	4.9	106	40	0.8535	190	N/A	25.36	635.5
04071052	NA	1	0.28	2.308	0	<1.0	0.015	12	7.1	45.3	40	0.8622	N/A	2386	28.17	643.0
04071072	NA	1	0.68	2.697	0	29.0	0.014	20	4.4	60.7	24	0.8665	168	N/A	36.91	608.1
04071073	NA	1	0.03	3.126	0	73.7	<0.010	14	7.3	21.1	39	0.8706	190	N/A	42.01	641.0
04071074	NA	1	0.34	3.568	0	46.9	<0.010	28	5.8	96.0	38	0.8627	119	N/A	56.69	645.8
04080015	NA	1	0.08	4.113	0	141.4	<0.010	32	6.3	128	35	0.8842	10	N/A	96.41	--
04080628	NA	1	0.42	4.858	0	55.1	0.024	40	3.9	215	35	0.8801	7	N/A	98.80	--

Appendix F: B20 Rancimat Results

Table 10. Rancimat Induction Time, Hours

SAMPLE ID	SwRI Replications			SwRI Bosch	AVG
	1	2	3		
B20R1	1.16	1.16	1.11	1.14	1.0
B20R2	>24	>24	>24	>24	-
B20R3	2.51	2.77	2.83	2.70	3.5
B20R4	16.13	16.03	17.46	16.54	20.3
B20R5	1.34	1.56	1.78	1.56	1.6
B20R6	0.6	0.73	0.66	0.66	0.9
B20R7	>24	>24	>24	>24	29.8
B20R8	1.03	1.63	0.52	1.06	1.4
B20R9	4.72	4.3	4.72	4.58	6.9
B20R10	3.45	4.84	4.93	4.41	5.9
B20R11	1.30	2.43	1.17	1.63	1.4
B20R12	4.62	2.81	2.90	3.44	7.7
B20R13	1.90	2.39	2.71	2.33	4.2
B20R14	0.68	0.69	0.73	0.70	1.3
B20R15	0.89	0.80	0.95	0.88	1.2
B20R16	2.65	3.10	2.65	2.80	3.9
B20R17	1.26	0.97	0.87	1.03	1.3
B20R18	5.83	5.55	5.17	5.52	7.0
B20R19	0.17	0.47	1.26	0.63	1.0
B20R20	1.35	0.67	1.19	1.07	1.3
B20R21	1.46	1.90	1.88	1.75	3.2
B20R22	0.90	0.79		0.85	1.5
B20R23	1.93	1.85		1.89	4.2
B20R24	4.84	5.86	7.23	5.98	16.8
B20R25	>24	12.88	>24	>24	9.8
B20R26	1.76	1.88	1.94	1.86	2.6
B20R27	0.57	0.53	0.79	0.63	1.1
B20R28	1.98	1.99	1.39	1.79	2.1
B20R29	1.72	1.7	1.6	1.67	2.7
B20R30	2.11	2.14	2.06	2.10	2.2
B20R31	6.55	6.26	6.86	6.56	12.4
B20R32	4.58	4.41	4.04	4.34	4.8
B20R33	1.68	1.64	1.64	1.65	2.1
B20R34	4.56	4.79	4.59	4.65	5.8
B20R35	0.88	1.51	1.41	1.46	1.6
B20R36	5.52	6.38	6.51	6.14	11.3

References

1. United States Department of Energy, Energy Information Agency, http://www.eia.doe.gov/cneaf/alternate/page/datatables/afvtable10_03.xls. Accessed May 12, 2005.
2. Knothe, G.; Dunn R.O. "Dependence of Oil Stability Index of Fatty Compounds on Their Structure and Concentration and Presence of Metals." *Journal of the American Oil Chemists' Society*; Vol. 80, 2003; p. 1021.
3. Brand-Williams, W.; Cuvelier, M.E.; Berset, C. "Use of a Free-Radical Method to Evaluate Antioxidant Activity." *Food Science Technology - Lebensm.-Wiss*; Vol. 28, 1995; p. 25.
4. deMan, J.M.; Tie, F.; deMan, L. "Formation of Short Chain Volatile Organic Acids in the Automated AOM Method." *Journal of the American Oil Chemists' Society*; Vol. 64, 1987; p. 1993.
5. European Committee for Standardization. *EN 14214: Automotive Fuels — Fatty Acid Methyl Esters (FAME) for Diesel Engines — Requirements and Test Methods*. 2003.
6. Westbrook, S. *An Evaluation and Comparison of Test Methods to Measure the Oxidation Stability of Neat Biodiesel: Final Report*. NREL/SR-540-38983. Work performed by Southwest Research Institute. Golden, CO: National Renewable Energy Laboratory, October 2005.
7. Neff, W. E.; Selke, E.; Mounts, T. L.; Rinsch, E. N.; Zeitoun, M. A. M. "Effect of Triacylglycerol Composition and Structures on Oxidative Germoplasm." *Journal of the American Oil Chemists' Society* ; Vol. 69, 1992; p. 111.
8. Cosgrove, J. P.; Church, D. F.; Pryor, W. A. "The Kinetics of the Autoxidation of Polyunsaturated Fatty Acids." *Lipids*; Vol. 22., 1987; p. 299.
9. Westbrook, S.R.; Stavinoha, L.L. "Biodiesel and B20 Blends: Stability Test Methods and Stability Characteristics," *IASH 2003, the 8th International Conference on Stability and Handling of Liquid Fuels*, Steamboat Springs, Colorado, September 14-19, 2003.
10. Lawrence, R. Results on biodiesel stability presented at the Biodiesel Technical Workshop, New Orleans, January 2003.

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) October 2005			2. REPORT TYPE Technical Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004					5a. CONTRACT NUMBER DE-AC36-99-GO10337	
					5b. GRANT NUMBER	
					5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) R.L. McCormick, T.L. Alleman, M. Ratcliff, L. Moens, and R. Lawrence					5d. PROJECT NUMBER NREL/TP-540-38836	
					5e. TASK NUMBER FC06.9400	
					5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393					8. PERFORMING ORGANIZATION REPORT NUMBER NREL/TP-540-38836	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10. SPONSOR/MONITOR'S ACRONYM(S) NREL	
					11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT (Maximum 200 Words) This document reports results gathered from quality surveys in 2004 of biodiesel (B100) and 20 percent biodiesel (B20) blends in the United States.						
15. SUBJECT TERMS biodiesel; biodiesel blends; B20, biodiesel quality; B100						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code)	

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18